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QUALITY CONTROL AND NONDESTRUCTIVE EVALUATION TECHNIQUES FOR
COMPOSITES - PART I: OVERVIEW OF CHARACTERIZATION TECHNIQUES
FOR COMPOSITE RELIABILITY

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PREFACE

This project was accomplished as part of the U.S. Army Aviation Research and Development Command Manufacturing Technology program. The primary objective of this program is to develop, on a timely basis, manufacturing processes, techniques, and equipment for use in production of Army materiel. Comments are solicited on the potential utilization of the information contained herein as applied to present and/or future production programs. Such comments should be sent to: U.S. Army Aviation Research and Development Command, ATTN: DRDAV-EGX, 4300 Goodfellow Blvd., St. Louis, MO 63120.

The work described in this report was accomplished under a contract monitored by the Army Materials and Mechanics Research Center. Technical monitor for this contract was Dr. R. J. Shuford.

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1.0 INTRODUCTION

Advanced composite materials technology has undergone a fundamental transition in the last decade and is now implemented in a wide range of large scale primary structures ranging from composite helicopter rotor blades to composite cargo bay doors for Space Shuttle orbitor. Part of this technology development for composite reliability is a highly organized advancement in the methods and management of characterization methodologies. These characterization methodologies can be listed in the approximate order of their implementation as follows:

1. Chemical Quality Assurance Testing
2. Processability Testing
3. Cure Monitoring and Management
4. Nondestructive Evaluation (NDE)
5. Performance and Proof Testing
6. Durability Analysis and Service Life Prediction

This overview will discuss the detailed characterization methods in the context of the management concept for implementing the specific tests.

Chemical analysis, nondestructive evaluation (NDE) and environmental fatigue testing of composites generates three classes of information on composite reliability which needs to be integrated in a reliability analysis. Several new management methodologies for accomplishing this result are reviewed and discussed. The rapid evolution of computer aided design and manufacturing (CAD/CAM) places new emphasis on automated monitoring and feed-back control during both the manufacture and service usage of composite materials. The idealized feed-back control signal from an NDE monitoring system is a structural margin of safety indicator. Computer models for composite durability and environmental fatigue presently contain margin of safety predictions. A major challenge for characterization methodologies is the development of practical structural margin of safety monitoring systems which operate in the structure during manufacture and service.

The results of a recent overview survey concerning "Chemical Characterization for Composite Reliability" will be presented for discussion and comment. This survey interrogates the available reference literature, and evaluates the most important current and future characterization methods.

2.0 THE SCOPE OF CHARACTERIZATION

Characterization begins with materials selection and continues through manufacture and use of a composite material. The logic flow chart of Fig. 1 shows a typical predictive design methodology which begins on the left with system definition and ends on the right with an accept or reject decision for the manufactured part. The logic flow of Fig. 1 shows that materials selection occurs as an early step in component design. Requirements for materials improvement are also shown in Fig. 1 to be closely linked to component design, life prediction and materials selection. Physical property data on commercial polymers is extensively tabulated but is generally limited to performance and proof test data developed under ASTM or DIN standard methods. For example, a single publisher systematically compares over 16,000 polymeric materials including adhesives, plastics, foams, films, sheets and laminates, and composite prepregs.^(1,2) This discussion is specifically addressed to fiber reinforced composite characterization and covers the full range of special topics from initial quality acceptance of prepreg constituents to durability analysis and service life prediction of the reinforced composite structure. A recent encyclopedic review provides a comprehensive presentation of commercially available fiber reinforced prepregs and cured laminates with extensive compilations and ranking of performance and proof test properties of composites.⁽²⁾

The scope of this discussion is defined by the detailed listing of characterization methods presented in Table 1. The classification and methods listing of Table 1 includes thirteen test methods for chemical quality assurance, processability, and cure monitoring. An additional 13 tests describe nondestructive evaluation (NDE) and a more extensive list of 47 ASTM-DIN

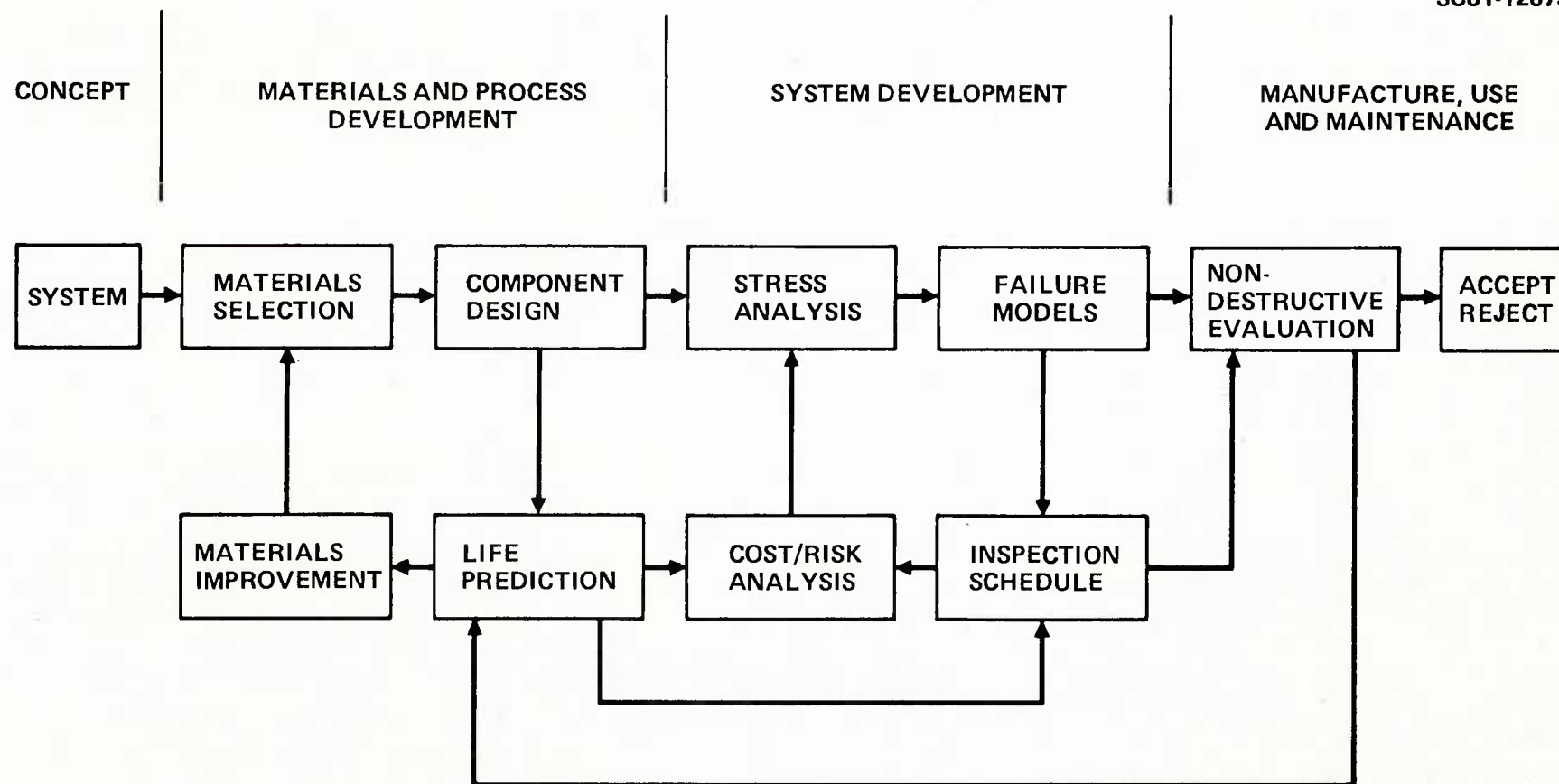


Fig. 1 Logic flow chart for predictive design methodology.

Table 1

Detailed Listing of Characterization Methods

1. Chemical Quality Assurance
 1. HPLC (high performance liquid chromatography)
 2. GC/MS (gas chromatography/mass spectroscopy)
 3. FTIR (Fourier transform infrared spectroscopy)
 4. NMR (nuclear magnetic resonance spectroscopy)
 5. Elemental Analysis
 6. Surface Analysis
2. Processability Testing
 1. DSC (differential scanning calorimetry)
 2. TMA (thermal mechanical analysis)
 3. DMA (dynamic mechanical analysis)
 4. TGA (thermal gravimetric analysis)
 5. SEA (surface energy analysis)
3. Cure Monitoring and Management
 1. Temperature/Pressure/Vacuum
 2. AC Dielectrometry
 3. DC Conductivity
 4. Acoustic Emission
4. Non-destructive Evaluation
 1. US (ultrasonic) immersion C-scan reflector plate
 2. US immersion C-scan through transmission
 3. US contact through transmission
 4. US contact pulse-echo
 5. Fokker bond tester
 6. 210 sonic bond tester
 7. Sondicator
 8. Harmonic bond tester
 9. Neutron radiography
 10. Low KV x-ray
 11. Coin tap test
 12. Acoustic emission
 13. Thermography
5. Surface NDE
 1. Ellipsometry
 2. Surface Potential Difference (SPD)
 3. Photoelectron Emission (PEE)
 4. Surface Remission Photometry (SRP)

Table 1 (continued)

6. Performance and Proof Testing

ASTM-DIN Test Equivalents

The following presents a listing of the properties of plastics reported in this book, the ASTM numbers and the equivalent DIN tests:

	Units of Measure			Test	
	English	Metric	SI	ASTM	DIN
<u>Processing</u>					
1 Processing Methods	°F	°C			
2 Comp'n Molding Temp	°F	°C			
3 Inject Stock Melt Temp	°F	°C			
4 Extrusion Temp	°F	°C			
5 Bulk Factor				D1895	D[53466]
6 Linear Mold Shrinkage	in/in			D955	D[53464]
7 Melt Flow		g/10 min		D1238	D[53735]
8 Melting Point	°F	°C			
9 Density	lb/ft ³	g/cm ³	Mg/m ³	D792	D[53479]
10 Specific Volume	in ³ /lb	cm ³ /g	m ³ /Mg	D792	D[53479]
<u>MECHANICAL PROPERTIES</u>					
11 Tensile Str. yield	10 ³ lb/in ²	10 ² kg/cm ²	MPa	D638	
12 Tensile Str. break	10 ³ lb/in ²	10 ² kg/cm ²	MPa	D638	D[53455]
13 Tensile Str. low temp	10 ² lb/in ²	10 ² kg/cm ²	MPa	D638	D[53455]
14 Tensile Str. high temp	10 ³ lb/in ²	10 ² kg/cm ²	MPa	D638	D[53455]
15 Elongation %, yield				D638	D[53455]
16 Elongation %, break				D638	D[53455]
17 Tensile Modulus	10 ⁵ lb/in ²	10 ⁴ kg/cm ²	GPa	D638	D[53457]
18 Flexural Str. yield	10 ³ lb/in ²	10 ² kg/cm ²	MPa	D790	D[53452]
19 Flexural Modulus	10 ⁵ lb/in ²	10 ⁴ kg/cm ²	GPa	D790	D[53457]
20 Stiffness in Flex.	10 ⁵ lb/in ²	10 ⁴ kg/cm ²	GPa	D747	
21 Compressive Str.	10 ³ lb/in ²	10 ² kg/cm ²	MPa	D695	D[53454]
22 Izod. notched R.T.	ft lb/in	kg cm/cm	kJ/m	D256	
23 Izod. low temp	ft lb/in	kg cm/cm	kJ/m	D256	
24 Hardness	(test)				

Table 1 (continued)

	Units of Measure			Test	
	English	Metric	SI	ASTM	DIN
<u>THERMAL PROPERTIES</u>					
25 Thermal Conductivity	BTU in/hr ft ² °F	10 ⁻⁴ cal/sec cm ² °C/cm	W/Km	C177	D[52612]
26 Specific heat	BTU in/hr ft ² °F	cal/g °C	kJ/kg K	C351	
27 Linear Therm Expan	10 ⁶ in/in °F	10 ⁻⁵ mm/mm °C	K	D696	D[52328]
28 Vicat Soft Point	°F	°C		D1525	D[53460]
29 Brittle Temp	°F	°C		D746	
30 Continuous Svc Temp	°F	°C			
31 Defl Temp 264 lb/in ² , 18.5 kg/cm ² , 1.81 MPa	°F	°C		D648	D[53461]
32 66 lb/in ² , 4.6 kg/cm ² , 0.45 MPa	°F	°C		D648	D[53461]
33 U.L. Temp Index		°C/mm			
<u>ELECTRICAL PROPERTIES</u>					
34 Volume Resistivity		Ohm cm		D257	D[53482]
35 Surface Resistivity		Ohm		D257	D[53482]
36 Insulation Resistance		Ohm		D257	D[53482]
37 Dielectric Strength	V/10 ⁻³ in	kV/mm	MV/m	D149	D[53481]
38 Dielectric Constant: 50-100 Hz				D150	D[53483]
39 10 ² Hz				D150	D[53483]
40 10 ⁴ Hz				D150	D[53483]
41 Dissipation Factor: 50-100 Hz				D150	D[53483]
42 10 ³ Hz				D150	D[53483]
43 10 ⁴ Hz				D150	D[53483]
<u>OPTICAL PROPERTIES</u>					
44 Refractive Index, Sodium D				D542	D[53491]
45 Clarity					
<u>ENVIRONMENTAL PROPERTIES</u>				D570	D[53473]
46 Water Absorp. %, 24 hr				D570	D[53473]
47 Equil Water Content %				D570	D[53473]
7. Durability Analysis and Service Life Prediction (Some Current Programs)					
1. U.S. Army Composite Materials Research Program (AMMRC).					
2. AFML, "Processing Science of Epoxy Resin Composites, Contract No. F33615-80-C-5021.					
3. AFML/ARPA, "Quantitative NDE, Contract No. F33615-74-C-5180.					
4. AFML, "Integrated Methodology for Adhesive Bonded Joint Life Predictions F-33615-79-C-5088.					

equivalent tests define standard performance and proof testing. Section 7 of Table 1 lists several of the current research programs for durability analysis and service life prediction.

The concepts of characterization are reviewed in several general references.⁽³⁻⁷⁾ Billmeyer⁽³⁾ presents the general principles of polymer chemistry and introduces the essential definitions of polymer physical chemistry measurement which are essential to this discussion. The discussion of Kaelble⁽⁴⁾ develops and combines the subject of chemistry, adhesion and polymer rheology into models of composite response which are essential to this discussion. The proceedings of several recent ACS (American Chemical Society) symposiums review the state of progress in resins for aerospace⁽⁵⁾ and physical characterization methods.⁽⁶⁾ The specific effects of service environments on composite materials has been recently reviewed in an AGARD conference proceedings and this report adequately assesses the current status of proof testing and service life prediction.⁽⁷⁾

3.0 POLYMER PHYSICAL STATES AND TRANSITIONS

It is useful to define five potential physical states for components of polymer composites which are:

- vapor (v) - involving volatile or condensible components, generally of low molecular weight
- liquid (l) - involving the flow state where interchain entanglements or crosslinks do not inhibit macromolecular motion.
- rubber (r) - involving free motion of polymer segments with superposed restriction of macromolecular motion by interchain entanglements and crosslinks
- glass (g) - involving the formation of an amorphous solid state with restricted rotational motion of short chain segments.

crystalline (c) - involving the first order transition to a crystalline solid state with restricted rotational and vibrational motion of short chain segments.

In discussing thermal or rheological transitions from one to another of these five states there is often a confusion as to both the type of transition and time direction of transition from initial to final state. For this discussion we will adopt a nomenclature which details both the type and direction of transition. For example the following transition temperatures are:

T_{lv}	=	from liquid (l) to vapor (v)
T_{vl}	=	from vapor (v) to liquid (l)
T_{gr}	=	from glass (g) to rubber (r)
T_{rg}	=	from rubber (r) to glass (g)
T_{rl}	=	from rubber (r) to liquid (l)
T_{lr}	=	from liquid (l) to rubber (r)

During curing it is often shown that the path of cure involves changes from liquid to rubber to glass to rubber with the following sequence of transition temperatures T_{lr} , T_{rg} , T_{gr} . The detailed time-temperature-transformation state diagrams discussed by Gillham⁽⁸⁾ illustrates these multiple transitions and the potential value of the above definitions.

A detailed listing of characterization methods for composites is presented in Table 1. In later sections each of these methods will be discussed in more detail. The standard units and conversion factors associated with these methods are listed in Table 2. A brief pictorial review of polymer characterization is shown in Figs. 2 - 6 which may clarify the interrelations between these numerous test methods.

The upper view of Fig. 2 shows the chemical degree of polymerization (left ordinate) versus degree of cure (abscissa). The polymer is soluble up

Table 2
Standard Units and Conversion Factors

ASTM TEST DESCRIPTIONS AND UNITS				
To Convert		To Convert		To Convert
Metric Units	Multiply By	Si Units	Multiply By	English Units
g/cm ³	1.0	Mg/in ²	0.016	lb/ft ³
kgf/cm ²	10.194	MN/m ² or MPa	0.0069	lb/in ²
kgf/cm ²	10.194	MN/m ² or MPa	0.0069	lb/in ²
kgf/cm ²	10.194	MN/m ² or MPa	0.0069	lb/in ²
kgf/cm ²	10.194	MN/m ² or MPa	0.0069	lb/in ²
kgf/cm ²	10.194	MN/m ² or MPa	0.0069	lb/in ²
kgf/cm ²	10.194	MN/m ² or MPa	0.0069	lb/in ²
kgf cm/cm	10.194	kJ/in	0.0534	ft lb/in
kgf cm/cm	101.936	kJ/m ²	0.021	ft lb/in ²
cal/sec cm C	23.88	W/K m	0.144	BTU in/hr ft ² F
cal/g C	0.239	kJ/kgK	4.187	8TU/lb F
cm/cm C	1.0	m/m K	1.8	in/in F
kV/mm	1.0	MV/m	0.0394	V/10 ⁻³ in
ASTM TEST DESCRIPTIONS AND UNITS				
To Convert		To Convert		To Convert
Metric Units	Multiply By	Si Units	Multiply By	English Units
g/cm ³	1.0	Mg/in ²	0.016	lb/ft ³
kgf/cm ²	10.194	MN/m ² or MPa	0.0069	lb/in ²
kgf/cm ²	10.194	MN/m ² or MPa	0.0069	lb/in ²
kgf/cm ²	10.194	MN/m ² or MPa	0.0069	lb/in ²
kgf/cm ²	10.194	MN/m ² or MPa	0.0069	lb/in ²
kgf/cm ²	10.194	MN/m ² or MPa	0.0069	lb/in ²
kgf/cm ²	10.194	MN/m ² or MPa	0.0069	lb/in ²
kgf cm/cm	10.194	kJ/in	0.0534	ft lb/in
kgf cm/cm	101.936	kJ/m ²	0.021	ft lb/in ²
cal/sec cm C	23.88	W/K m	0.144	BTU in/hr ft ² F
cal/g C	0.239	kJ/kgK	4.187	8TU/lb F
cm/cm C	1.0	m/m K	1.8	in/in F
kV/mm	1.0	MV/m	0.0394	V/10 ⁻³ in

$$^{\circ}\text{F} + ^{\circ}\text{C} = (^{\circ}\text{F} - 32) : 1.8$$

$$^{\circ}\text{C} + ^{\circ}\text{F} = (^{\circ}\text{C} \times 1.8) + 32$$

$$^{\circ}\text{C} + ^{\circ}\text{K} = ^{\circ}\text{C} + 273.15$$

Special names and symbols for a few typical SI units are listed below:

The following table lists SI units prefixes for decimal multiplication and submultiples:

Quantity	Name	Symbol	Factor	Prefix	Symbol
frequency	Hertz	Hz	10 ¹⁸	exa	E
power	Watt	W	10 ¹⁵	peta	P
electrical/resistance	Ohm	Ω	10 ¹²	tera	T
electrical/potential	Volt	V	10 ⁹	giga	G
force	Newton	N	10 ⁶	mega	M
pressure	Pascal	Pa	10 ³	kilo	k
energy, work	Joule	J	10 ²	hecto	h
length	meter	m	10 ¹	deka	da
mass	kilogram	kg	10 ¹	deci	d
time	second	s	10 ⁻²	centi	c
thermodynamic/temperature	Kelvin	K	10 ⁻³	milli	m
			10 ⁻⁶	micro	μ
			10 ⁻⁹	nano	n
			10 ⁻¹²	pico	p
			10 ⁻¹⁵	femto	f
			10 ⁻¹⁸	atto	a

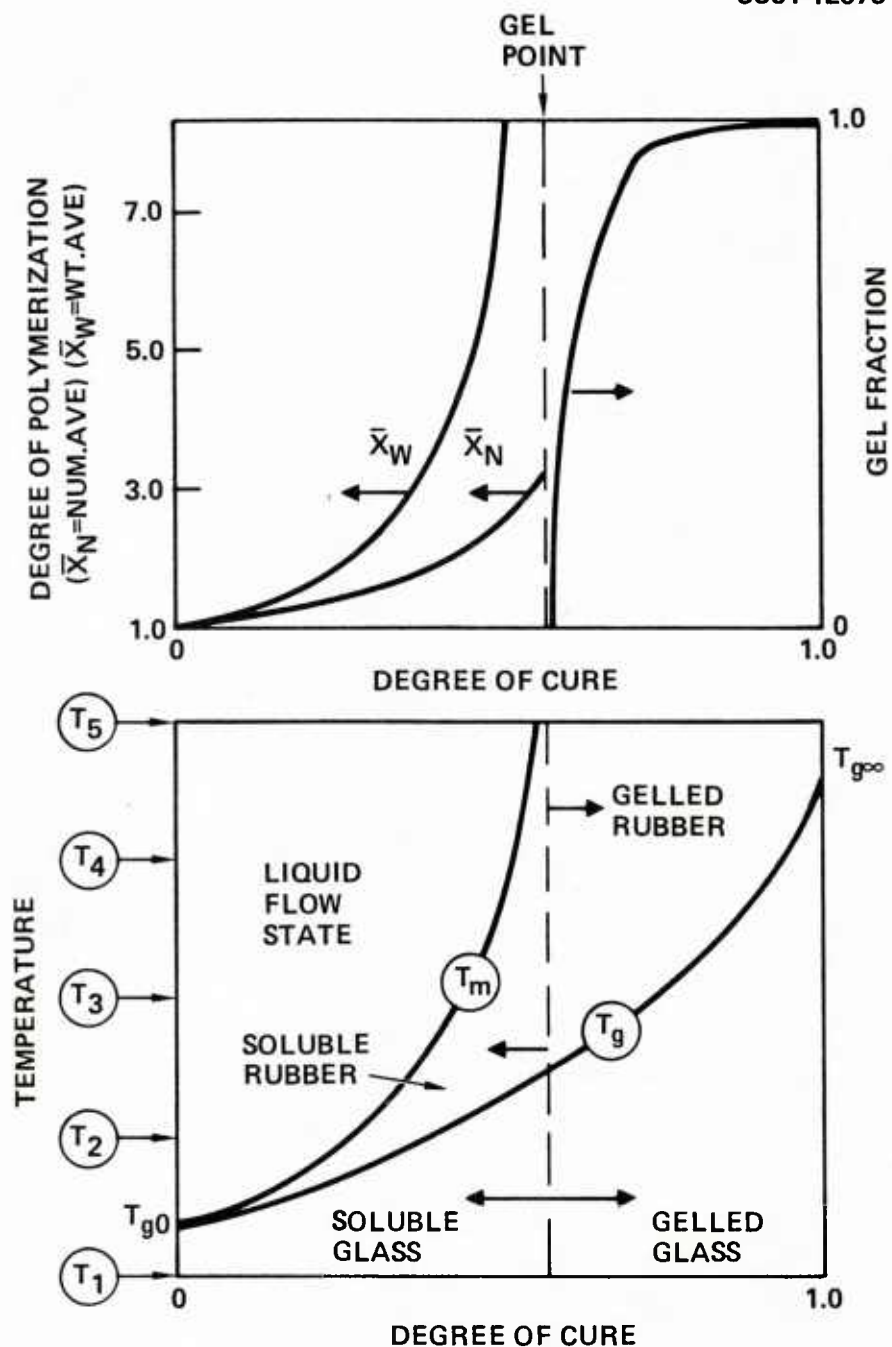


Fig. 2 (Upper): Change in molecular weight distribution and sol-gel state with degree of cure (idealized).
 (Lower): The effect of degree of cure upon glass transition temperature T_g and melt temperature T_m for liquid flow (idealized).

to the gel point. The breadth of the molecular weight distribution is measured by the ratio of weight to number average molecular weight \bar{X}_w/\bar{X}_n which is termed the heterogeneity index of molecular weights. At the gel point the weight average molecular weight, which describes the larger molecules of the polymer, approaches infinity. Further increase of the degree of cure beyond this gel point causes a rapid rise in the insoluble fraction termed gel formed by the crosslinking of these large molecules. At complete cure the gel fraction should constitute the bulk of the polymer with negligible unreacted low molecular polymer. The chemical quality assurance tests in upper Table 2 are exploited to verify the chemical changes graphed in upper Fig. 2.

The curves in lower Fig. 2 outline the characteristic changes in rheological states of liquid flow, rubber, and glass which shift the flow temperature T_m and glass temperature T_g with degree of cure. The lower limit of the liquid flow state extends down to the monomeric glass temperature T_{go} . The uncured resin does not possess a rubbery state at zero degree of cure. With increasing degree of cure the lower cures of Fig. 2 show the appearance of a soluble rubbery state which separate the flow state from the soluble glass state. The transition between flow and rubbery state, termed T_m , rises to the limits of thermal stability as the degree of cure approaches the gel point. In cure processing, the elimination of bubbles, entrapped air, and unwetted interface by manipulation of pressure and vacuum must all be accomplished in the flow state and prior to gelation. The gelled polymer has an infinite viscosity and will not flow. At a degree of cure beyond the gel point only the gelled rubber and gelled glass states exist.

Processability tests which measure both thermal and rheological transitions are shown in upper Table 2. These tests use small samples of polymer in fully instrumented experiments to define the appearance of characteristic changes in physical properties. The right margin of lower Fig. 2 identifies five scan temperatures, T_1 to T_5 , for isothermal monitoring of the degree of cure.

The curves of lower Fig. 2 show that the glass transition T_g rises with degree of cure to a final value $T_{g\infty}$ for the fully cured polymer of infinite molecular weight. This shift in T_g with degree of cure is the fundamental change in properties which produces the structural stiffness and strength for the cured polymer.

The idealized isothermal dynamic mechanical monitoring of the degree of cure for the degree of cure for the five temperatures $T_1 - T_5$ is shown in Fig. 3. The lowest temperature T_1 is below T_{g0} and therefore monitors the glass state throughout cure. The upper curve of Fig. 3 plots the nearly constant value of the glass state storage modulus G' and shows cure state does not influence this property. The remaining curves of upper Fig. 3 show the characteristic rise in $\log G'$ to the glass state value as the increasing degree of cure raises first T_m and then T_g through the constant monitoring temperatures $T_2 - T_5$. In the flow state where, for example T_2 is greater than T_m , the expected value of G' , which measures the elastic energy of dynamic deformation, should be zero.

The lower curves of Fig. 3 plot the idealized trends in the loss tangent $\tan \delta = G''/G'$ where G'' is the loss modulus and a measure of the flow energy dissipated during dynamic deformation. At the low temperature T_1 , the polymer is glassy at all states of cure and $\tan \delta$ is unaffected by state of cure. At the higher temperatures $T_2 - T_5$ where cure starts in the liquid flow state the ideal value of $\tan \delta$ should be infinity since $G' = 0$ and then decrease to the glass state value with increased state of cure as shown in lower Fig. 3. The first knee on the $\log G'$ and $\log \tan \delta$ curves of Fig. 3 is specifically associated with the liquid to rubber transition T_{lr} rising through the isothermal test temperature. The second knee on the curves of Fig. 3 is associated with the rubber to glass T_{rg} rising through the isothermal monitor temperatures $T_2 - T_5$. Since T_5 is slightly above $T_{g\infty}$, as shown in Fig. 2, the full transition to glass state dynamic response is not obtained at full cure.

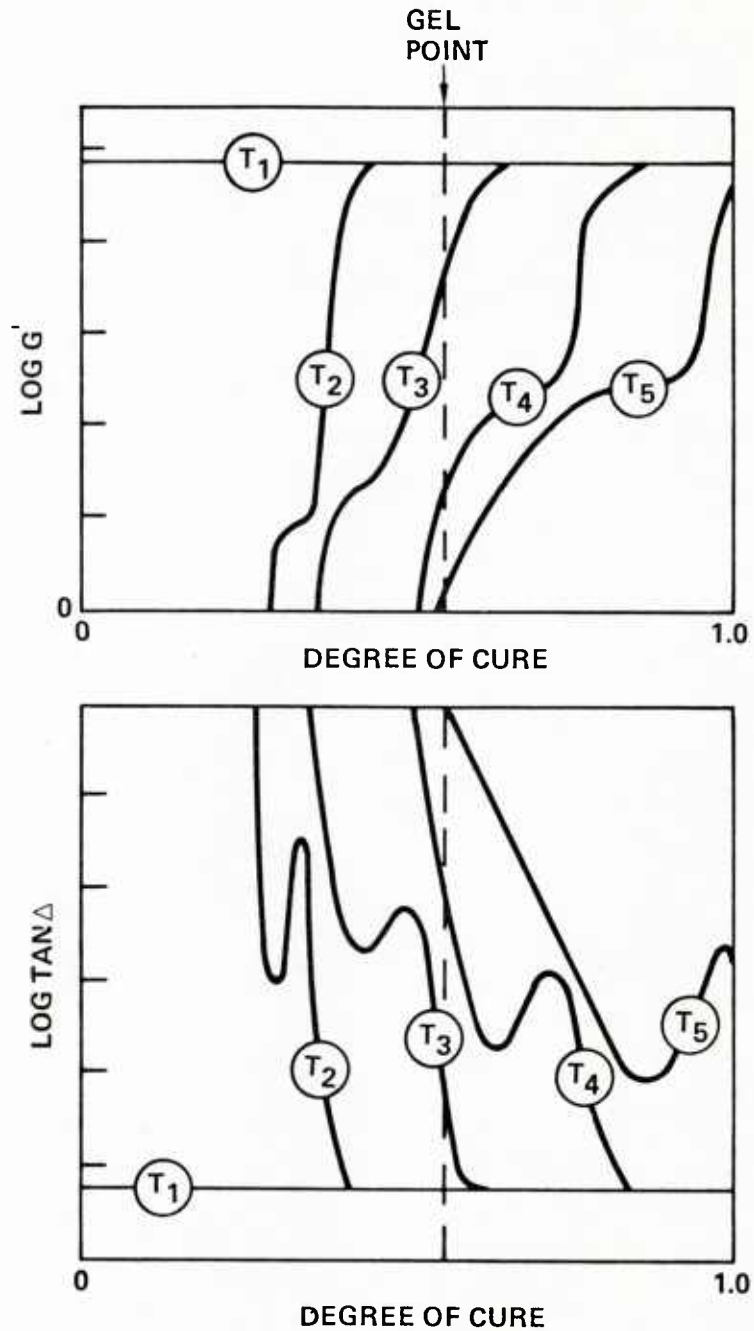


Fig. 3 Idealized isothermal dynamic mechanical monitoring of degree of cure in terms of shear storage modulus G' (upper view) and loss tangent ($\tan \delta$ (lower view)).

In category 3 of Table 2 the common cure monitor tests such as AC impedance (dielectrometry) and DC resistance measure rheological properties which relate in a fairly direct way to the curves of Fig. 3. The fundamental problem in cure monitoring and cure process management is the reconstruction of the more fundamental chemical and physical information graphed in Fig. 2 from cure monitoring data. Optimum process control of temperature, pressure, and vacuum conditions for cure can be visualized as being more direct from data shown in Fig. 2 than Fig. 3.

Consider now that cure is complete as shown by the properties at the right ordinate of Figs. 2 and 3. The upper curve of Fig. 4 shows the idealized thermal scan of tensile modulus E from well below the glass temperature $T_g = T_{g\infty}$ of the fully cured resin. The types of molecular motion typically available below and above T_g are shown in upper Fig. 4. The flow temperature T_m shown in Fig. 4 is taken to be associated with high temperature chemical decomposition with network scission to produce a new high temperature flow state. The alternative thermal decomposition process would involve thermal decomposition with additional cross linking which would tend to raise T_g and produce a brittle solid without available network segment motion.

For the cured resin with network segment motion available above T_g the lower curves of Fig. 4 show three domains of tensile stress versus temperature response at constant loading time. The lower diagram of Fig. 4 shows that both T_g and T_m are reduced by applied tensile stress. A number of theories concerning stress or pressure effects on rheological response indicate the physical state zones defined in lower Fig. 4. The region to the left of the T_g curve is the brittle solid state and when stress rises past the solid failure stress σ_b a brittle fracture is predicted. The intersection of the T_g and σ_b curves defines the brittle temperature T_b above which plastic yielding can occur.

Tensile stressing above T_b provides a tensile yield stress when the stress penetrates the T_g curve of lower Fig. 4 and craze fracture when stress

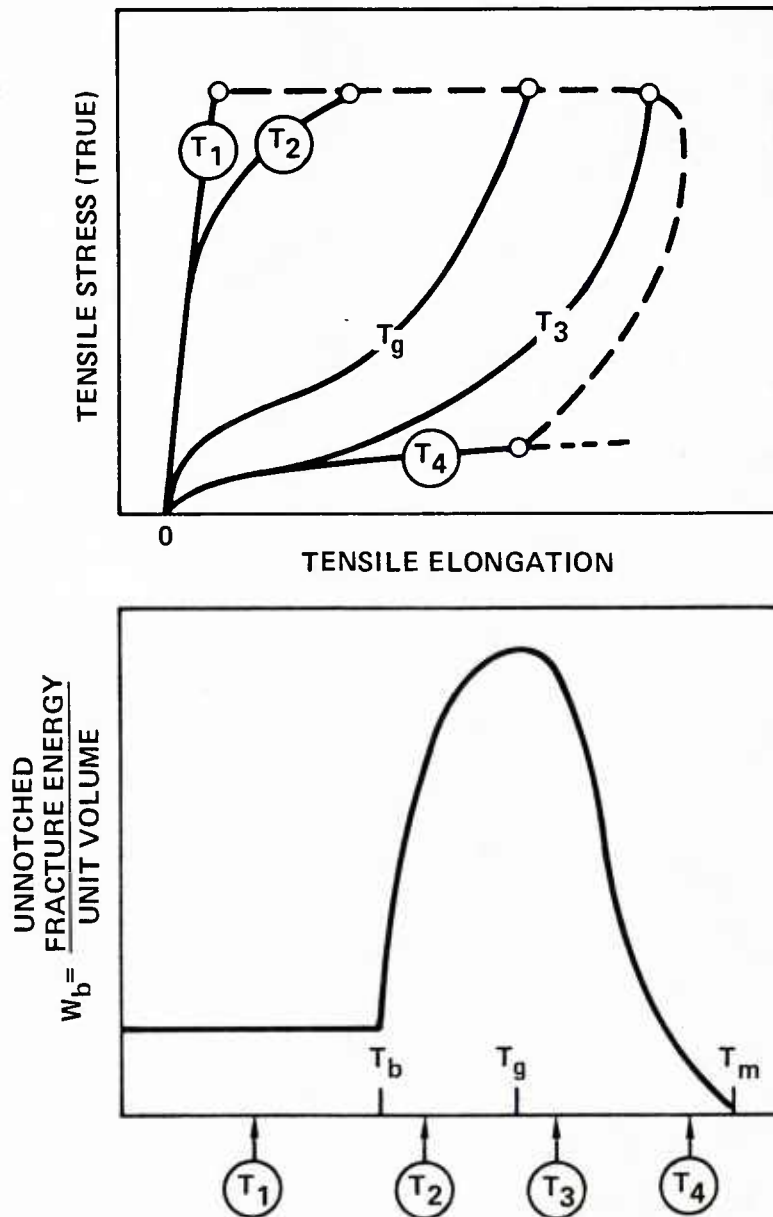


Fig. 4 Thermal scanning of fully cured matrix for tensile modulus (upper view) and stress-temperature response (lower view) at constant time of loading (idealized).

exceeds σ_b . At a higher temperature in lower Fig. 4 such as T_4 the stress can rise through the T_m curve and produces a flow failure mechanism. Idealized stress versus strain curves for the four temperatures $T_1 - T_4$ plus T_g in lower Fig. 4 can be drawn to illustrate these points. The fundamental point illustrated in lower Fig. 4 is that stress and temperature interact to produce characteristic transitions from brittle to rubber to flow states. These stress-temperature transitions in mechanical response fundamentally affect mechanical performance and structural integrity.

The upper view of Fig. 5 sketches the expected form of the tensile stress versus strain curves. The stress is represented as the true stress of the deformed cross-section to retain the connection with the curves of lower Fig. 4. The area beneath the related curves of nominal stress (of the undeformed area) versus strain define the unnotched fracture energy per unit volume W_b shown by the temperature curve of lower Fig. 5. The lower curve of Fig. 5 is typical of many structural polymers which display maximum toughness near T_g . The temperature span of high fracture toughness is one of the distinct features of engineering thermosets such as epoxy resins and thermoplastics such as the polycarbonates.

The stress strain curves of upper Fig. 5 show the typical shapes shown by engineering plastics. At T_g or higher temperature the upward curvature reflects chain orientation effects which in some polymers are quite pronounced. At the highest temperature, T_4 , failure is visualized as caused by a tensile cold drawing which is characteristic of filamentary orientation of cavities at crack tips in fracture mechanics specimens.

The utilization of the thermomechanical responses shown in Fig. 4 and Fig. 5 in fracture mechanics and stress analysis models is illustrated in the curves of Fig. 6. The upper curve of Fig. 6 illustrates an elastic-plastic analog curve which is fit to an experimentally measured polymer stress versus strain response. The analog (dashed) curve has the same curve area, since $A_1 = A_2$ and the same strength and extensibility end point as measured by repetitive testing and statistical analysis. For fracture mechanics analysis for

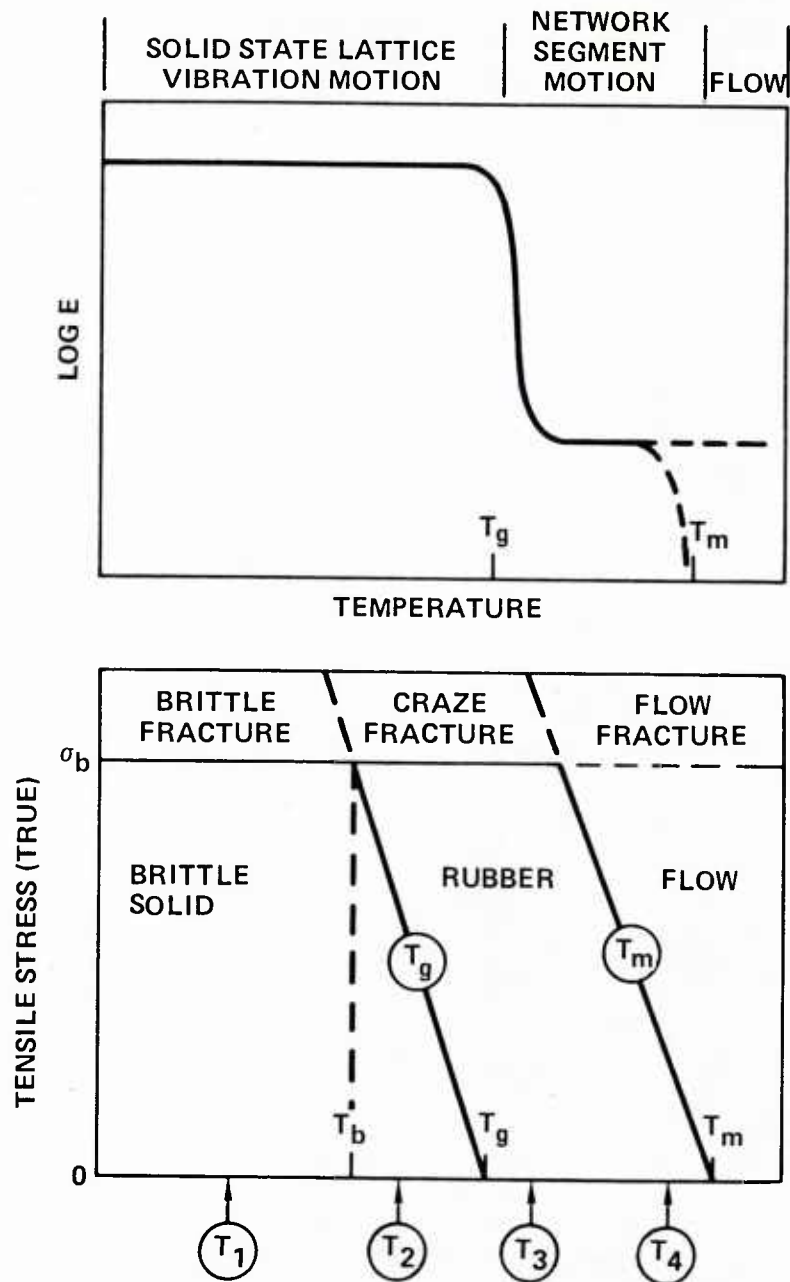
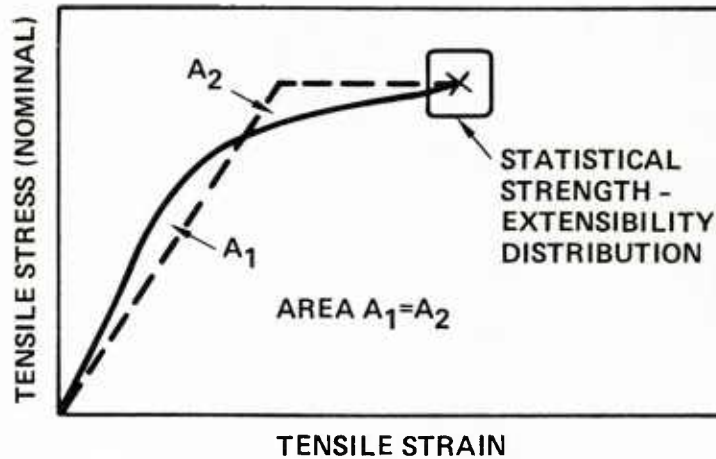
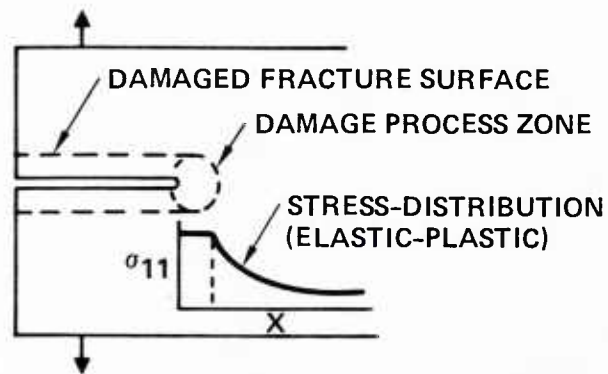


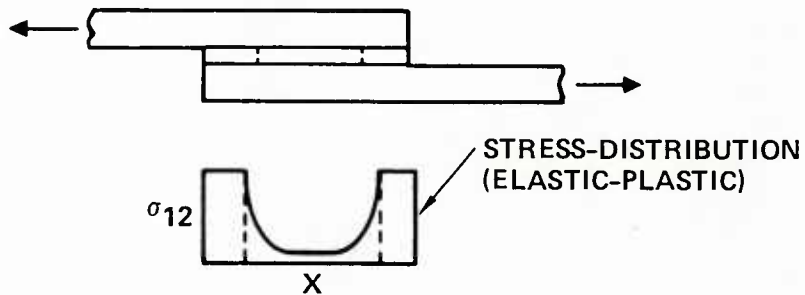
Fig. 5 Characteristic tensile stress-strain and fracture response (upper view) and temperature profile of unnotched tensile fracture energy (lower view).



I. ELASTIC-PLASTIC ANALOG STRESS-STRAIN CURVE



II. FRACTURE MECHANICS (DUGDALE MODEL)



III. STRESS ANALYSIS (HART-SMITH MODEL)

Fig. 6 Conversion of measured stress-strain to elastic-plastic analog (I) and introduction into fracture mechanics (II) and stress analysis (III) predictive models.

crack growth this elastic-plastic analog is introduced into the Dugdale⁽⁸⁾ model shown in the middle view of Fig. 6. For stress analysis this elastic-plastic analog is introduced into typical Hart-Smith models⁽⁹⁾ for adhesive joints design as shown in lower Fig. 6.

The two lower views of Fig. 6 thus incorporate all of the data of Table 2 into either fracture mechanics or stress analysis models. Durability analysis and service life prediction studies outlined in part 7 of Table 2 utilize mechanics models of this type. The more sophisticated fracture mechanics and stress analysis models currently under development utilize the curvilinear stress strain response pictured in the upper curve of Fig. 6 to obtain greater computational precision.

4.0 CHEMICAL QUALITY ASSURANCE

One essential objective in chemical quality assurance testing is verifying the lot-to-lot reproducibility of material constituents in composite prepregs. Each prepreg chemistry may require a complete development of a chemical quality assurance program. The flow chart for chemical analysis illustrated in Fig. 7 involves a sequence of chemical separations combined with quantitative chemical analysis of each of the separated components. The flow chart of Fig. 7 was developed by Carpenter and Bartels⁽¹¹⁾ for analysis of selected types of 350°F (177°C) service ceiling epoxy matrix composite prepregs and adhesives. Chemical characterization programs for composite prepregs are reported by May, Helminiak and Newey⁽¹²⁾ which implement a similar approach of successive molecular separation followed by quantitative chemical analysis. The separation methodologies implemented in the analysis of epoxies depends largely upon solvolytic separation by HPLC combined with infrared spectroscopy and elemental analysis. Quite a different approach has been employed by Alston⁽¹³⁾ in chemically analysing fully cured PMR-15 polyimide-graphite composites by use of thermo-oxidative degradation combined with Fourier transform IR and NMR analysis of degradation products.

Table 3

Detailed Listing of Characterized Properties

1. Chemical quality assurance
 1. Chemical composition
 2. Degree of cure
 3. Molecular weight distribution
 4. Number average molecular weight
 5. Weight average molecular weight
 6. Entanglement molecular weight
2. Processability
 1. Gel point
 2. Gel fraction
 3. Crosslink molecular weight
 4. Glass temperature
 5. Melt (flow) temperature
 6. Dynamic storage modulus
 7. Dynamic loss modulus
3. Cure Monitoring
 1. Temperature/pressure/vacuum
 2. Dynamic dielectric constant
 3. Dielectric loss factor
 4. DC conductivity
4. Nondestructive evaluation
 1. Internal stress distributions
 2. Damage zone size
 3. Crack growth rate.
5. Performance and Proof testing
 1. Stress and environment dependant T_g
 2. Stress and environment dependant T_m
 3. Isothermal stress-strain-time response
 4. Strength distribution
 5. Extensibility distribution
 6. Fracture energy distribution
6. Combined bonding and failure testing
 1. Surface energy
 2. Surface chemistry
 3. Surface morphology
 4. Surface roughness

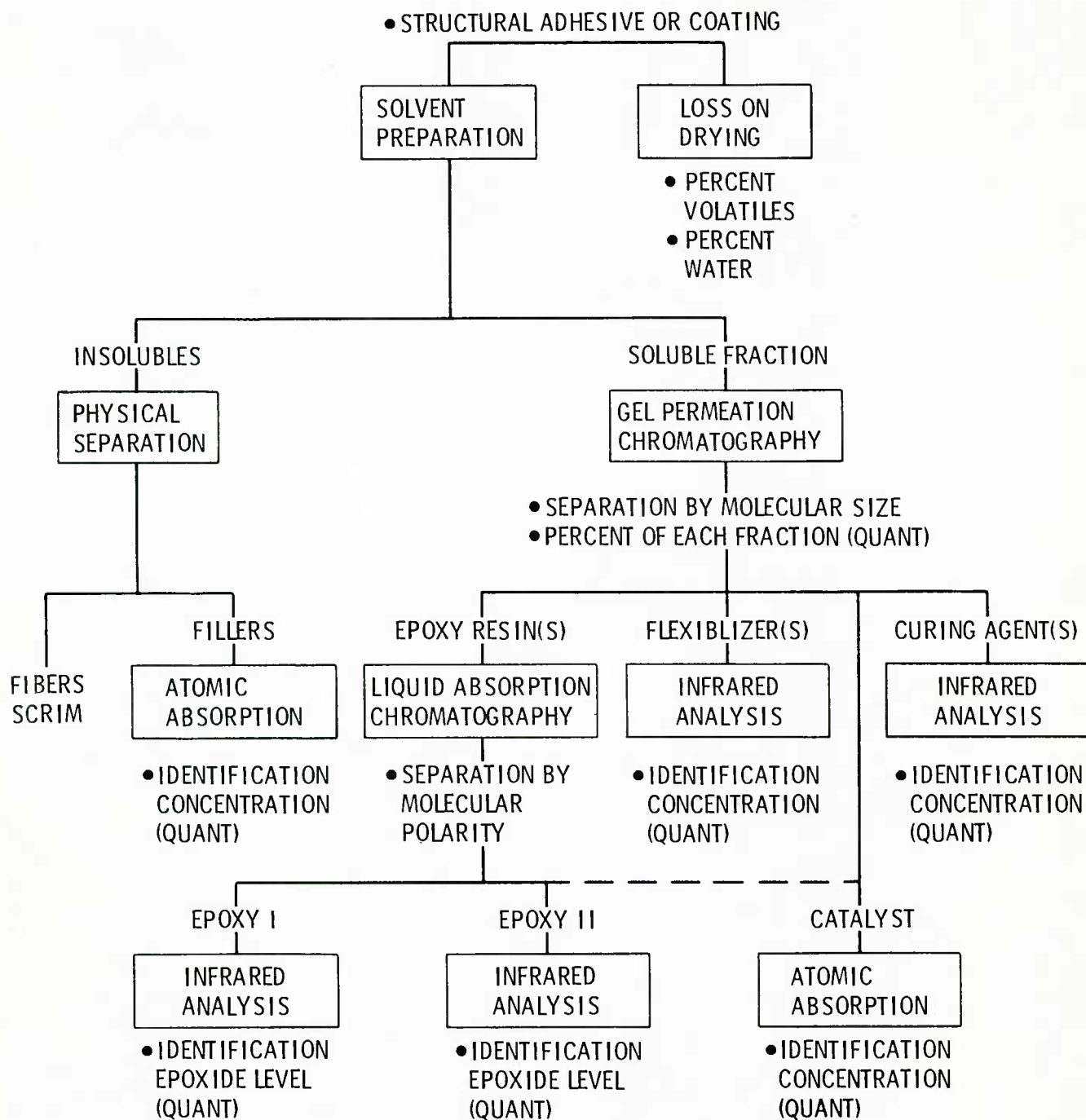


Fig. 7 Chemical analysis flow chart.

Several recent reports describe and demonstrate interdisciplinary approaches for composite characterization which incorporate chemical characterization, adhesion criteria, and composite durability analysis in a unified characterization scheme.⁽¹⁴⁻¹⁶⁾ These early attempts to integrate chemical quality assurance into a general composites durability evaluation follows the strategy suggested by Fig. 1. A recent special issue of the journal "Polymer Composites" presents a collection of papers which summarize the central position of chemical characterization in the U.S. Army composite materials research program.⁽¹⁷⁾

What follows are brief summaries and descriptive references to the chemical quality assurance test methods listed in Table 1. Gas and liquid chromatography form a class of molecular separation methodologies and these are classified into ten categories in Table 4 according to the description of McNair.⁽¹⁹⁾ Surface characterization methods for reinforcing fiber coatings also fall into nine or more categories in Table 5 and these are classified according to ability to detect specific surface properties.^(19a)

The advantages and limitations for each of the six test methods for chemical quality assurance are listed below with detailed references provided for each method. Surface characterization methods are further subdivided as outlined in Table 5.

1. HPLC (High Performance Liquid Chromatography)^(18,19,20)

Advantages: Quick separations in seconds to minutes. Very high resolution of 100 or more components. Provide easily performed quantitative analysis with errors less than 1%. Very small sample size with measurements of 10^{-9} to 10^{-12} g reported. Analyses a wide variety of sample types - molecular weights from 18 to 6 million g/mole can be measured. Measurements largely automated.

Limitations: Requires high-resolution column and high-pressure pump. Instruments are expensive. Extensive experience of 6-12 months

Table 4

Classification of Chromatographic Methods

- I. Gas Chromatography (GC)
 - Gas liquid (GLC)
 - Gas solid (GSC)
- II. High performance liquid chromatography (HPLC)
 - A. Planar Chromatography
 - Thin layer (TLC)
 - Paper (PC)
 - B. Column Chromatography
 - Exclusion (EC)
 - Gel Permeation (GPC)
 - Gel filtration (GFC)
 - Liquid-solid or adsorption (LSC)
 - Liquid-liquid or partition (LLC)
 - Bonded phase (BPCO)
 - Ion exchange (IEC)

From: H. M. McNair, American Laboratory, May 1980, pp. 33-44.

Table 5
Decision Matrix of Surface Characterization Methods for
Reinforcing Fiber Coatings (35 to 70 nm thickness)

	Coating Durability	Molecular Orientations	Surface Concentration of Components	Surface Coating Uniformity	Fiber Curvatures	Adhesion Strength	Thickness Uniformity	Average Coating Thickness	Row Ave.
4 = Excellent									
3 = Acceptable									
2 = Marginal									
1 = Unacceptable									
0 = No Information									
Surface Energy Analysis	3	4	3	4	4	2	1	1	2.75
Scanning Elect. Mic. + EDAX	4	1	1	4	4	1	4	1	2.5
Electron Spect. for Chem. Anal.	4	4	4	1	1	1	1	1	2.13
ASTM Adhesion Test	4	1	1	1	1	4	1	1	1.75
Fourier Transform IR	2	2	3	1	1	1	1	1	1.50
Optical Microscopy	1	1	1	1	1	1	1	1	1.0
Secondary Ion Mass Spec.	1	1	1	1	1	1	1	1	1.0
Laser Microprobe Mass Analyser	1	1	1	1	1	1	1	1	1.0
Raman Microspectroscopy	1	1	1	1	1	1	1	1	1.0
Col Ave.	2.33	1.78	1.78	1.67	1.67	1.44	1.33	1.00	

required for proficient operation. HPLC is a poor identifier with other instruments such as mass spectrometer required to identify each peak. There is no universal and sensitive detector. Refractive index detectors are universal but has limited sensitivity. Ultraviolet detectors are sensitive but selective. This method is limited to soluble materials.

2. GC/MS (Gas Chromatography/Mass Spectroscopy)^(21,22)

Advantages: Pyrolysis combined with gas chromatography and mass spectroscopy provides a means for direct chemical separation and analysis of insoluble and crosslinked polymers. Controlled pyrolytic breakdown of macromolecular structures furnishes a profile of gas chromatographic peaks for mass spectrum analysis. Recently introduced Fourier transform MS (Nicolet FTMS-1000) increases the speed and resolution of the pyrolytic analysis methodology.

Limitations: Method is quite expensive with a price tag of \$300,000 for a computerized FTMS system.

3. FTIR (Fourier Transform Infrared Spectroscopy)⁽²²⁻²⁵⁾

Advantages: The high resolution (generally less than 1.0 cm^{-1}) combined with rapid (2-20s) scanning of the IR spectrum makes this a versatile method for chemical analysis. The computer assisted addition and subtraction of reference spectra permit direct isolation of molecular volatile lose, and specific chemical reactions. Reflectance IR can be combined with transmission measurements to provide a variety of sampling methodologies. Kinetics of curing reactions can be measured by FTIR. Combined with molecular separation techniques such as HPLC the versatility of FTIR is greatly extended.

Limitations: There are few limitations to this method and its versatility is a continuing challenge to the analyst.

4. Nuclear Magnetic Resonance⁽²⁶⁻²⁷⁾

Advantages: Proton, ^{19}F and ^{13}C NMR provide important methods for defining the short range stereochemical structure of monomers and polymers. Over the last decade ^{13}C NMR has assumed increasing importance in defining tacticity, comonomer sequence, cis-trans isomerism, branching and cross-linking. High resolution ^{13}C NMR in the solid state is now achieved using proton dipolar decoupling, magic angle spinning and $^1\text{H} - ^{13}\text{C}$ cross polarization. Where applicable ^{19}F NMR shows high sensitivity to tacticity.

Limitation: Many of the newer ^{13}C techniques are still under development and therefore not amenable to routine use in chemical characterization.

5. Elemental Analysis^(22,28)

Advantages: The atomic ratios of C, N, O, Si, P, S, H and the halogens F, Cl, Br, I provide essential information in identifying the organic chemistry of composite materials. Routine elemental analysis is now largely carried out quantitatively in automated commercial instruments (such as the Perkin-Elmer Model 240-B). Atomic adsorption spectroscopy supplements conventional elemental analysis to permit highly sensitive (parts per million sensitivity) and quantitative analysis for over 35 metallic elements. Atomic adsorption (AA) spectroscopy is particularly useful in detecting organo-metallic catalysts which modify the processability of thermosetting resins.

Limitations: Elemental analysis provides no direct information on molecular structure other than the empirical formula for molar ratio of the elements and must be supplemented by other chemical structure analysis methods.

6. Surface Chemistry Analysis^(19a,29,30)

6.1 Wettability and Surface Energy Analysis (SEA) via Scanning Wilhelmy Plate Method

Advantages: Measures fiber circumference, estimates surface roughness and component surface concentrations, sensitive to coating removal, indirectly measures surface energies and environmental durability, digital recording permits statistical analysis of wetting forces and predicted adhesion.

Limitations: Sensitive to swelling, liquids analysis complicated by contact angle hysteresis, may emphasize low energy elements of surface chemistry in advancing contact angle, gives no direct chemical information.

6.2 Scanning Electron Microscopy (SEM) + Energy Dispersive X-ray (EDAX)

Advantages: Combined high resolution ($\sim 100\text{\AA}$) and great depth of focus, resolves unevenly distributed coatings, combined low voltage ($\sim 1.0\text{ keV}$), low magnification and TV scan can bypass metal coatings.

Limitations: Requires high vacuum and consequent volatiles loss, may cause charging and require metal coatings, EDAX signal from thin ($\sim 70\text{ nm}$) coatings too weak for analysis.

6.3 Electron Spectroscopy for Chemical Analysis (ESCA)^(34,35)

Advantages: Small sampling depth ($\sim 50\text{ nm}$) ideal for thin coating analysis, most used elements can be detected and elements (C,N,O) show changes in binding energy with oxidation state, x-ray does not damage the surface, coating thickness can be evaluated by varying take-off angle.

Limitations: Requires high vacuum and consequent volatiles loss, depth profiling restricted by damage produced by ion beams, geometry of fibers and fiber bundles creates problems.

6.4 ASTM Adhesion Tests⁽³⁶⁾

Advantages: Gives direct measure of apparent bond strength, gives direct measure of durability in terms of strength degradation, can be used to generate reliability statistics for mechanical design.

Limitations: Measures a system response as opposed to an interface property, no direct chemical information, results depend on joint design and test method.

6.5 Fourier Transform Infrared Spectroscopy (FTIR) & Internal Reflection and Attenuated Total Reflectance (ATR)⁽³⁷⁻³⁹⁾

Advantages: Little sample preparation, provides direct chemical identification of thicker coatings, digital recording of spectrum provides basis for extended data processing, rapid multiscans increase signal to noise, difference spectra analysis isolates chemistry of thin (~35 nm) coatings with reflective strong-absorbance bands.

Limitations: Penetration depth of IR radiation is much larger than typical coating thickness (~ 35 nm), absorption bands at longer wave length are enhanced by greater depth penetration.

6.6 Optical Microscopy

Advantages: Little sample preparation, records color and birefringence, can scan large areas.

Limitations: Low resolution (~ 1 μm), limited depth of focus at high magnification, does not resolve curved surfaces, nor show evenly distributed coatings, no chemical information.

6.7 Secondary Ion Mass Spectroscopy (SIMS)⁽⁴⁰⁾

Advantages: Small sampling depth (~ 10Å), potentially broad range of secondary ions can be analysed .

Limitations: Requires high vacuum and volatiles loss, the high energy inert gas ions which bombard the fiber surface cause degradation and pyrolysis thus rendering this method nonoperative on polymeric fibers.

6.8 Laser Microprobe Mass Analysis (LAMMA)⁽⁴¹⁾

Advantages: Provides analysis of a small fiber area (1 μm diameter), time-of-flight mass analyser defines secondary ions, limited depth of analysis ($\sim 0.1 \mu\text{m}$), possible to map surface, small sample volume (10^{-19} gm).

Limitations: Requires high vacuum with volatiles loss, the laser energy output produces disintegration of the fiber without isolating coating constituents.

6.9 Microprobe Molecular Optics Laser Examiner (MOLE) or Raman Microscopy^(42,43)

Advantages: Records Raman spectrum from a small area ($\sim 1\mu\text{m}^2$), does not require high vacuum so can analyse volatiles, in principle can locate and analyse for coating surface distribution.

Limitations: Requires strong Raman scatterers in coating and weak scatterers in fiber, in thin coatings the dominant sampling volume will come from the fiber.

5.0 PROCESSABILITY TESTING

Laboratory tests for composite processability are designed to determine how a sample performs during a simulated manufacturing cure cycle. In general, these tests use small quantities of material (from 0.01 to 1.0 gm), are fully instrumented, and operated by programmed scanning of temperature at constant scan rate. The four thermal analysis methods listed under processability testing in Table 1, part 2, are highly complementary and are normally marketed as components of a thermal analysis system (such as Mettler

TA 2000, DuPont 900, and Perkin-Elmer DSC-2). Recent studies and comparison on the several commercial systems are provided by Wunderlich and coworkers.⁽⁴⁴⁾ The function of processability testing is to define the kinetics of curing, the limits of thermal stability, and the optimum cure cycle which leads to high performance and durability. Very often, procedures of chemical analysis such as outlined in Fig. 7, are implemented to verify thermal analysis data and to define the chemical mechanisms of curing. Composite matrix polymers are commonly classified in terms of their temperature range of cure processing or the service ceiling temperature for environmental stability. The earlier discussion of Figs. 2-6 has already introduced the multiple changes induced in thermal and rheological response as a consequence of curing. Considering the complexity of curing processes it is not surprising that logic flow diagrams, such as discussed by Kaelble,⁽¹⁶⁾ and shown in Fig. 8 have been developed to better integrate processability testing with evaluation of composite performance and durability.

The upper portion of Fig. 8 describes two forms of thermal analysis, DSC (differential scanning calorimetry) and TMA (thermal mechanical analysis) as central components of processability testing. These combined tests characterize the degree of cure and the effect of cure on the melt temperature T_m and glass temperature T_g as shown by the lower view of Fig. 2. By clever design of the commercially available accessories for thermal analysis systems many of the ASTM performance and proof tests listed in category 6 of Table 1 can be simulated using small samples (0.01 to 0.10 g) in a highly instrumented thermal analysis measurement. The function of processability testing is to find the optimum processing "window" which is a combination of processing times, temperatures, and pressures which both consolidate, form by flow, and chemically cure the composite laminate. These processability studies should always be accompanied by relevant chemical analysis.

The processing of laminates and fiber reinforced composites inevitably involves interface bonding during the process cycle. The utilization of wettability tests and surface energy analysis (SEA) is a subject well

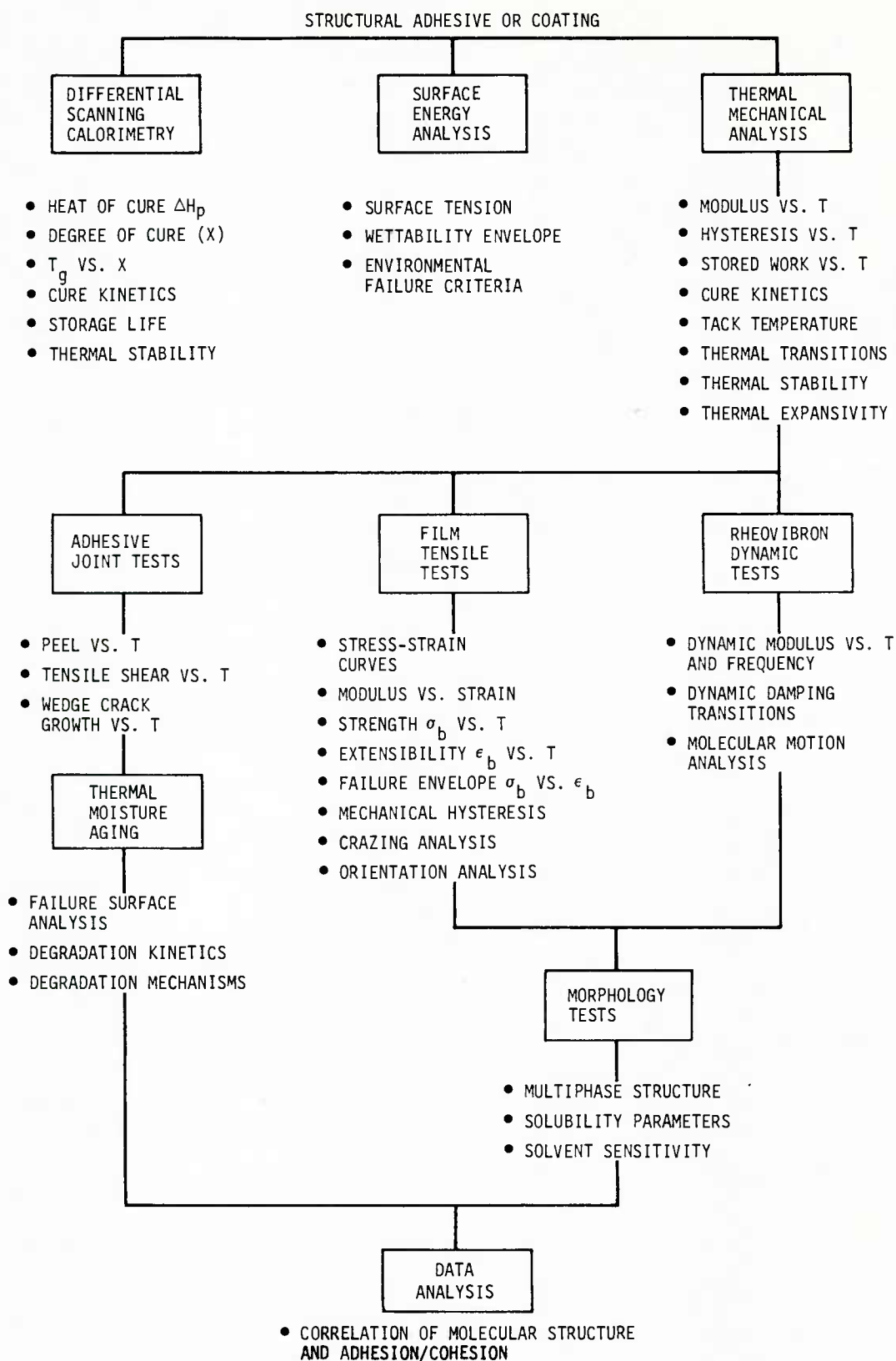


Fig. 8 Physical and mechanical analysis.

developed in the field of adhesive bonding but still largely overlooked in fibrous composite process evaluation. Rather extensive interface integrity studies sponsored by the Army Composites Research Program⁽¹⁷⁾ and the Air Force Materials Laboratory⁽¹⁴⁾ strongly support the implementation of SEA in conjunction with thermal analysis. SEA involves the testing of solid surface wettability by contact angle measurements with a selected set of test liquids. The analysis which accompanies SEA testing gives predictions of bonding ability and bond durability of the composite interface.

Brief descriptions of the commonly used processability test methods listed in Table 1 are presented in terms of advantages and limitations as follows:

1. Differential Thermal Analysis (DTA)⁽⁶⁾

Advantages: Measures the temperature difference (ΔT) between sample and reference under programmed thermal scan. High ($\Delta T < 0.001^\circ\text{C}$) sensitivity, wide range of high temperature and pressure, and small sample size, and measurement simplicity are advantages.

Limitations: Generally applied in qualitative analysis, calibrations and data processing are required to determine heats of reactions or specific heat properties of sample. DSC accessories are available to simplify direct evaluation of thermal properties.

2. Differential Scanning Calorimetry (DSC)^(6,45)

Advantages: Directly measures the rate of heat release (dH/dt) or absorption of a sample relative to a reference specimen. Measurements provide quantitative measure of heat of reaction ΔH (to 3%) and heat capacity (to 0.5%) properties under isothermal or constant thermal scan rates (up to $50^\circ\text{C}/\text{min}$), directly measures thermal state of cure x , cure kinetics, and cure effects on glass transition T_g .

Limitation: Less sensitive and more limited temperature and pressure ranges than DTA.

3. Thermal Mechanical Analysis (TMA)⁽⁶⁾

Advantages: Measures a sample thermal expansion or penetration softening under isothermal or constant rate thermal scan conditions and adjustable mechanical load. Operates as a modular accessory to DTA and TMA. High displacement sensitivity (0.025 μm) and dilatometer accessories permit small scale simulation of ASTM thermal and mechanical tests. Often used in conjunction with DTA, DSC, and TGA.

Limitations: In general, the physical limitations of accessory modes of measurement for penetrometry, dilation and tensile creep limit the quantitative precision of the "nominal" thermal response measurement.

4. Thermal Gravimetric Analysis (TGA)^(6,45)

Advantages: Measures sample weight changes due to volatile loss and thermal decomposition under isothermal or constant thermal scan rate. Detects chemical reactions which change sample weight which cannot be sensed by other methods. High precision (0.1%) and sensitivity (0.01 mg) with small sample size (≈ 10 mg). Often used in conjunction with DTA, DSC, or TMA and can be augmented by chemical analysis such as GC/MS.

Limitations: Weight change measurement needs additional modes of characterization to identify the process chemistry or physics.

5. Surface Energy Analysis (SEA)^(31-33,46-49)

Advantages: Tests for bonding ability by liquid-solid contact angle measurement. Method is quantitative and simple to apply. A thermogravimetric analysis (TGA) can be applied to provide automatic measure of advancing and receding contact angle on fibers and sheets at controlled temperature or programmed temperature change. Adhesive bonding and interface durability

parameters can be calculated. Method extends and quantifies ASTM tests for surface quality assurance.

Limitations: Method is limited to continuous surfaces, and high microroughness introduces contact angle hysteresis. Interface solubility and chemical reactions limit the surface energy analysis. Small samples required for TGA method and small drops and microscope for large surface analysis. See Table 5 for comparative sensitivities.

6. Dynamic Mechanical Analysis (DMA)⁽⁵⁾

Advantages: Isolates the storage (elastic) and loss (viscous) components of rheological response at varied frequency, temperature, and state of cure. Methods applicable to unsupported polymer or polymer supported by braid. Highly sensitive to both the flow T_m and glass T_g transitions at all states of cure. A primary laboratory tool with DSC for defining optimum cure process conditions.

Limitations: No single DMA method is universally applicable so multiple DMA methods are generally required which cover the varied ranges of liquid to solid response. Quantitative interpretation requires concurrent chemical analysis.

6.0 CURE MONITORING AND MANAGEMENT

This section is concerned with feasible methods for direct in situ monitoring of cure during press or autoclave molding processes typical of composite production. The related subject of cure management is the utilization of the cure monitor in a closed loop control of the production cure process through the program time (t) versus cure temperature (T), external pressure (P), and internal degassing vacuum (V) imposed on the curing part. Information for "real time" management of this (t-T-P-V) program for production process control can derive from three sources which are:

1. Prior chemical analysis
2. Prior processability testing
3. Current cure monitor data from within the curing part.

The U.S. Army Composites Research Program provides extensive documentation of the combined utilization of the above three approaches to cure management⁽⁵¹⁻⁶⁰⁾ of epoxy-glass and epoxy-graphite composites. In these Army studies of matrix resins, prepregs, and composites the minimum chemical analysis includes HPLC (high performance liquid chromatography) and FTIR (Fourier transform infrared spectroscopy) used both individually and jointly as quality assurance tests to verify chemical reproducibility. The minimum processability testing is by DSC (differential scanning calorimetry) to verify the reproducibility of the curing kinetics. The characteristics of the epoxy resins which can be determined by these prior tests are degree of cure, aging of prepreg, effect of cure conditions on the oxidative stability of the resin, products of degradation attack, and effect of processing on the resin chemistry.⁽⁵¹⁾ This information can be exploited to optimize the cure cycle to accomodate variability in resin chemical composition and prepreg aging.

Four methodologies of cure monitoring are listed in Table 1. The first is the direct measure and recording of process temperature, pressure, and vacuum conditions which follow from the time cycle used to control the cure molding process. These above measurements are augmented by single or joint monitoring of AC dielectrometry, DC conductance, and acoustic emission within the curing part.⁽⁵¹⁾ Th advantage and limitations of these three cure monitoring methods are as follows:

1. AC Dielectrometry⁽⁶¹⁻⁶⁶⁾

Advantages: Close relations exist between AC dielectrometry and DMA response. Commercial instrumentation is available with adequate range and sensitivity of measurement. New microcircuitry is being developed for in situ measurement. Frequency scanning can be exploited in dielectric spectrum analysis and in feed-back control logic for process management.

Limitations: Changes in spacing between electrodes can modify the dielectric output. Increasing the number of prepreg plys between electrodes lowers measurement reliability. In some cases electrodes must be placed in bleeder layers outside the curing part.

2. DC Resistance^(51,64)

Advantages: Very simple electrical circuit. Resistance variations appear to correlate with storage component of dynamic modulus.

Limitations: No physical model correlating DC resistance and rheology is available.

3. Acoustic Emission⁽⁵¹⁾

Advantages: Acoustic emission sensors provide direct information on microcracking processes which occur in the cured composite during improper cool down. This signal can be exploited to control cool down and minimize internal microdamage and internal thermoelastic stresses.

Limitations: This method is new and needs further development. Physical interpretation of the monitor output also needs further study.

In principal, the sensors for all three of the above cure monitors could remain in the cured part for utilization in nondestructive evaluation (NDE) in service. Current reports indicate that AC dielectric monitoring of large autoclave molded parts is feasible, and within limits, can be applied in process control.^(66,67) It is evident that cure monitoring and management involves the intelligent incorporation of prior chemical analysis and processability test data. Computerized monitoring and automated cure management are currently under intensive development.

7.0 NONDESTRUCTIVE EVALUATION (NDE)

Nondestructive evaluation has recently emerged as a new branch of material science which concentrates in the area of nondestructive testing and analysis to determine residual reliability and durability of manufactured parts. By adopting new modes of computer controlled three dimensional scanning, the ultrasonic response parts with complex surface curvatures can be automatically mapped for flaws.⁽⁶⁸⁾ Ultrasonic inspection is often restricted by the necessity of providing liquid acoustic couplants between the US transducer and the test specimen. For metal containing substrates the use of electromagnetic induction to launch and detect ultrasonic waves across an air gap permits high speed inspection using electromagnetic acoustic transducers (EMAT's).⁽⁶⁹⁾

Normally no nondestructive testing method presently employed can detect poor adhesion resulting in low bond strength. Poor bond quality produced on phosphoric anodized aluminum produced by oily contamination or surface damage of the oxide by rubbing with Kraft paper prior to bonding was not detected by standard ultrasonic inspection.^(70,71) The recent development of an automated ellipsometer for rapid optical scanning of treated metal surfaces has shown that both of the above types of surface defects can be detected and corrected prior to bonding as part of process monitoring.⁽⁷²⁾ It is thus evident that process monitoring combines with post production (NDE) to provide a viable reliability and durability test methodology for adhesive bonded structures. Surface NDE will be reviewed as a separate subject in the next section.

The studies of Hagemeier, Fassbender, and Clark^(70,71) form one of the most detailed assessments of conventional NDE methods for large area inspection of critical bond-line flaws in laminated structures. This study forms part of the Primary Adhesive Bonded Structure Technology Program (PABST) in which an adhesively bonded and highly loaded primary aircraft fuselage was designed, fabricated and proof tested for reliability and durability. Some specific objectives of the NDE portion of this program were as follows:

1. Define the common flaw types and locations.
2. Determine flaw behavior and growth rates under fatigue loading and hydrothermal exposure,
3. Assess the ability of NDE to detect flaws and monitor flaw growth rates.

The interaction of these three objectives provides the new and interesting depth to the capability assessment of the NDE method under item 3 in the above objectives. A brief description of the advantages and limitations of these standard NDE methods is presented as follows.

1. Ultrasonic NDE

Advantages: This method uses pulsed ultra sound at 2.25 to 10 MHz. Both contact and immersion techniques of inspection are employed using four specific test geometrics which are:

- a. immersion C-scan reflector plate
- b. immersion C-scan through transmission
- c. contact through transmission
- d. contact pulse echo.

These methods may be automated to produce plan view recordings (C-scans) using methods (a) and (b).

Limitations: The ultrasonic method suffers from destructive wave interference. The problem with destructive wave interference is that there is an appearance that elements of a laminate are unbonded when they are not.

2. Fokker Bondtester

Advantages: This tester operates on the principle of resonance impedance and is widely used in the aerospace industry. The instrument is calibrated to respond to a shift in frequency and amplitude between an unflawed specimen and a flawed or unbonded standard. For unbonds less than the diameter of the transducer the instrument response will vary between unflawed and unbonded

standard responses. In addition to detecting unbonds or voids this method can detect porosity. Empirical relationships have been shown between Fokker NDE quality readings and shear bond strength and porosity. The Fokker bondtester measures both amplitude and frequency shift to more fully characterize the flaw.

Limitations: This instrument operates in the low kilohertz range with consequent longer wavelength and lower inherent spatial resolution. The test specimen must be manually scanned and flawed areas manually marked.

3. NDT - 210 Bondtester

Advantages: The principle of operation is similar to the Fokker bondtester.

Limitations: This instrument has only an amplitude meter readout and is therefore more restricted than the Fokker bondtester in interpretation of flaw type.

4. Sondicator (detailed description not provided)

5. Shurtronics Harmonic Bondtester

Advantages: Induces an intrasonic wave in an electrically conductive (metallic) substrate through electromagnetic induction (14-15 KHz). A change in structural ultrasonic response is detected by a wide-band (28-30 KHz) receiving microphone. The instrument is calibrated to read just above zero for good structure and full scale for debonds 1/2 inch in diameter. This method does not require a liquid couplant.

Limitations: This method is limited to metallic structures and has limited sensitivity to first ply debonds.

6. Neutron Radiography

Advantages: Particularly useful when bonding components are not x-ray opaque. Can be used to detect voids and porosity. The hydrogen atoms in water and organic plastics are neutron opaque and therefore can be imaged in terms of intrusion and defects on neutron radiograms.

Limitations: Requires radiographic facility, generally used to supplement x-ray radiography.

7. X-ray Radiography

Advantages: Low voltage (25 to 65 KV) x-ray provides maximum contrast. This method is effective for complex geometries difficult to inspect ultrasonically. The method can be used to detect water intrusion. For honeycomb assemblies radiography is often a primary inspection method. Water intrusion into honeycomb is easily detected.

Limitations: This method is enhanced by use of x-ray opaque materials as adhesive and matrix components.

8. Coin Tap Test

Advantages: Tap testing with a coin or small aluminum rod is useful in locating large voids and disbonds of 1.5 in (3.7 mm) diameter or larger. The method is applicable for metal-metal or thin skin-honeycomb assemblies.

Limitations: The method is limited to the outer ply disbonds. The method is subjective and may yield variation in test results.

9. Acoustic Emission (Dunegan-301)

Advantages: The method uses a broad band (165 KHz) detector, 50 dB preamplifier, x-y recorder and a hot air gun to generate thermal stress in the part. The method detects wet interface corrosion delamination.

Limitations: To detect wet interface corrosion the detector transducer must be placed over the corroded area. Sensitivity is very dependant on both detector location and location of heat source.

10. Thermography

Advantages: Remote IR camera or liquid crystal coatings construct thermographic maps of a structural part undergoing current mechanical cycling or prior surface heating. The temperature map locates hot spots or cool spots which indicate locations of specific mechanical energy dissipation or thermal diffusivity differences indicative of stress concentrations or structural defects.

Limitations: The method is qualitative and requires physical interpretation by other measurements. The method is not applicable to metal skin laminates due to high thermal diffusivity.

The results of the study of Hagenauer and Fassbender⁽⁷⁰⁾ on the ability of NDE methods to detect defects in two types of bonded solid laminates is summarized in the decision matrix of Table 6. Each intersection of row and column in Table 6 is given a score which is 2 = defect detected, 1 = defect partially detected, and 0 = defect undetected. Nine types of defects which describe the rows of Table 6 are ranked relative to their row averaged scores decreasing from top to bottom. Twelve types of NDE methods which form the columns of Table 6 are ranked by decreasing column average score from left to right across the table. The best combination for high reliability flaw detection occurs in the upper left region of Table 6. The lower reliability sector of NDE methodology is identified in the lower right region of Table 6.

Both Table 6 and Table 7 show that voids are the most reliably detected type of defect. Thickness variations, and solid inclusions (separation sheet) are the least detectable types of defect in both solid and

Table 6
Decision Matrix Between Nondestructive Evaluation (NOE) Built-In
Defects in Laminate Panels

		Nondestructive Test (NDT) Method												Row Ave.
		(a) Immersion C-Scan Reflector Plate	(b) 210 Sonic Bond Tester	(c) Immersion C-Scan Through Transmission	(d) Fokker Bondtester	(e) Contact Through Transmission	(f) Contact Pulse-Echo Pulse-Echo	(g) Immersion C-Scan Pulse-Echo	(h) Sonicator	(i) Harmonic Bond Tester	(j) Neutron Radiography	(k) Coin Tap Test	(l) Low KV X-ray	
Built-In Defects In Laminate Panels	(1) Void	2	2	2	2	2	2	2	2	2	2	1	0	1.75
	(2) Void (C-14 repair)	2	2	2	2	2	2	2	2	2	2	1	0	1.75
	(3) Void (9309 repair)	2	2	2	2	2	2	2	2	2	2	1	0	1.75
	(4) Corroded Bond	2	2	2	2	2	2	1	1	1	2	1	2	1.67
	(5) Lack of Bond (skin to adhesive)	2	2	2	2	2	2	2	2	2	0	1	0	1.58
	(6) Porous Adhesive	2	2	2	0	2	2	2	0	2	2	0	2	1.50
	(7) Manufacturer's Separator Sheet	2	1	2	2	1	0	2	2	0	1	0	0	1.08
	(8) Burned Adhesive	2	2	2	2	2	2	1	0	0	0	0	0	1.08
	(9) Thick Adhesive (1, 2, 3 ply)	2	2	1	2	0	0	0	0	0	0	0	0	0.58
Col. Ave.		2.00	1.89	1.89	1.78	1.67	1.56	1.56	1.22	1.22	1.22	0.56	0.44	

Direction of Decreasing
Correlation:

0 = Defect Not Detected;

1 = Partial Detection;

2 = Detected

Table 7
Decision Matrix Between Nondestructive Evaluation
(NDE) Defects in Honeycomb Structures

		Nondestructive Test (NDT) Method												Row Ave.
		(a) Neutron Radiography	(b) Coin Tap Test	(c) Contact Through Transmission	(d) Immersion C-Scan Pulse-Echo	(e) Immersion C-Scan Through Transmission	(f) Fokker Bondtester	(g) Low KV X-Ray	(h) Harmonic Bond Tester	(i) 210 Sonic	(j) Sondicator	(k) Contact Pulse-Echo	(l) Contact Shear Wave	
Built-In Defects In Honeywell Structure	(1) Void (Foam to Closure)	2	2	2	2	2	2	2	2	2	2	2	0	1.83
	(2) Void (Adhesive to Skin)	2	2	2	2	2	2	2	2	2	2	2	0	1.67
	(3) Inadequate Tie-In of Foam to Core	2	2	2	2	2	2	2	2	2	2	0	0	1.50
	(4) Void (Adhesive to Core)	2	2	2	2	2	0	2	2	0	0	0	0	1.33
	(5) Separator Sheet (Skin to Adhesive	2	2	2	2	2	0	0	1	0	0	1	0	0.92
	(6) Water Intrusion	2	2	2	0	2	0	2	0	0	0	0	0	0.83
	(7) Crushed Core (After Bonding)	1	2	1	1	1	1	2	1	0	0	0	0	0.83
	(8) Inadequate Foam Depth At Closure	2	1	0	0	0	2	2	0	1	2	0	0	0.83
	(9) Separator Sheet (Adhesive to Core)	2	2	0	2	1	0	0	0	0	0	2	0	0.75
	(10) Chem-Mill Step Void	2	0	0	0	0	0	0	0	0	0	0	0	0.17
Col. Ave.		1.90	1.60	1.30	1.30	1.20	1.10	1.00	1.00	0.9	0.8	0.7	0	

Direction of Decreasing
Correlation: 0 = Defect
Not Detected; 1 = Partially
Detected; 2 = Detected

hollow core laminates. Dramatic new information is provided in intercomparing the scores of test methods in the solid laminate (Table 6) and skin stressed laminate (Table 7). For the solid laminate the ultrasonic test methods receive highest scores and display highest NDE reliability. For the skin stressed laminate (Table 7) neutron radiography and the coin tap test receive the highest detection rating. These studies clearly show that the reliability of an NDE method depends on both the type of structure (solid or hollow core) and the type of defect (void or inclusion) being studied. The decision matrix format provides a convenient means of identifying high reliability NDE methodologies with regard to test method, flaw type, and type of composite structure.

8.0 SURFACE NDE

Standard NDE methods as reviewed in the previous section, are not capable of defining poor interface quality which may lower the durability of a laminated composite structure. A new and rapidly developing area of surface NDE has recently emerged to fill this important gap in standard NDE methodology. Surface NDE methods are in general modifications of the tools of surface characterization to permit automation, rapid surface property mapping, and computerized data storage and processing. The objective of surface NDE is to perform a final inspection of surfaces to be bonded and to make accept-reject decisions on whether the surface will form a reliable - durable bonded joint or whether rejection and recycling through surface treatment is required.

The proceedings of a recent symposium on surface contamination edited by Mittal⁽⁷³⁾ provides an overview and detailed summaries of progress in this important emerging field of surface NDE. Very specific discussions of surface NDE are developed in this review.⁽⁷⁴⁾ In general, surface NDE falls into direct methods which directly identify the nature of the surface contaminant and indirect methods which identify contaminants through a surface property change. Direct methods for surface NDE have been reviewed under

surface chemical analysis and process monitoring. Indirect methods measure a surface property change which correlates with a specific class of surface degradation which lowers bond reliability and durability. Of the several indirect surface NDE measurements the following four methods have complementary advantages and limitations.

1. Ellipsometry^(73,77)

Advantages: The method is noncontacting and nondestructive. A beam of polarized monochromatic light is reflected from the surface. The phase shift of the reflected polarized light and reflection coefficients are analysed to measure surface roughness, contaminant film thickness (from 0.0 nm to 500 nm), and optical properties of the contaminant film. This method is automated and developed for rapid computer controlled surface mapping.

Limitations: Sensitivity is limited by the difference in refractive index of film and substrate. Maintaining the proper angle of incidence may require X-Y-Z indexing for curved surfaces.

2. Surface Potential Difference (SPD)⁽⁷³⁻⁷⁹⁾

Advantages: This method is non contacting and nondestructive. SPD is the difference between the work function of the test surface and a reference electrode and is extremely sensitive to the outer dipole layer of surface contamination. Commercial NDE instruments (Fokker contamination tester and Monroe Electronics ISO Probe) are available and computerized surface mapping has been developed.

Limitations: This method requires other measurements to make a physical interpretation of data. Electrode contamination and capacitance gap misalignment can affect the measurement.

3. Photoelectron Emission (PEE)(73-76)

Advantages: The method is sensitive to both substrate and surface film photoemission properties. It is extremely sensitive to thickness effects of electron attenuating contaminants. Methods for automation and surface mapping have been developed.

Limitations: Method requires an intense UV, (250 nm) light source. High sensitivity requires differences in photoemission properties of substrate and contaminant.

4. Surface Remission Photometry (SRP)

Advantages: Remission photometry permits surface spectral analysis at 200-800 nm wavelengths. The influence of surface roughness is small. The test surface is compared to a reference to minimize nonlinear spectral sensitivity of the photometer.

Limitations: Requires use of a light integrating sphere and twin beam optics. This method remains to be automated and computerized for rapid surface NDE mapping.

The combination of surface NDE and surface chemical analysis (see Tables 5) promises to provide a valid approach to reliability and durability analysis of structural adhesive bonding. At the moment surface NDE is an emerging technology which needs further development and integration of measurement and analysis methodologies to provide quantitative reliability and durability predictions.(23)

9.0 PERFORMANCE AND PROOF TESTING

Performance and proof testing of composite reliability by standard ASTM methods involves a group of 47 test methods as summarized in Part 6 of Table 1. These ASTM test methods fall into six categories of response which are: (2)

1. Processing
2. Mechanical Properties
3. Thermal Properties
4. Electrical Properties
5. Optical Properties
6. Environmental Properties.

A current and comprehensive set of brief descriptions of the advantages and limitations of these test methods are available.^(2,80) Rank ordered summaries of commercial prepreg and composite laminate properties as measured by these test methods are organized in tables for convenient reference and use in materials selection.⁽²⁾ The great importance of these ASTM performance and proof tests very largely relates to the fact they are commonly accepted and utilized thus providing a common fund of characterization data. Experience shows that ASTM tests used alone are an expensive and generally inadequate means of testing for composite reliability and durability. On the other hand, extensive quantitative characterization without ASTM testing provides a data base without a general technology reference. The appropriate solution is, of course, to design a test program based upon appropriate selection of the six test categories of Table 1 which fulfills the requirements of the generalized predictive design methodology shown in Fig. 1. Based upon the earlier discussion of physical states and transitions the minimum aim of performance and proof testing is to verify the predictions generated from chemical analysis and nondestructive evaluation. The detailed listing of significant characterized properties proposed in Table 3 also summarizes the critical types of properties required from performance and proof testing. A full understanding of the stress and environment dependent glass temperature T_g and flow temperature T_m is essential in terms of performance and proof test conditions. The connection of T_g and T_m characterization by ASTM methods and micro characterization techniques form an important logic link between scientific characterization and end-use testing. The utilization of standard ASTM tests to establish the isothermal stress-strain-time response is essential to

fully define the mechanical responses graphically outlined in Figs. 4-6 in end-use related test geometries. Finally, the statistical distributions of strength, extensibility, and fracture energy are required for defining statistical margins of safety in stress analysis and strength analysis of predict reliability and durability. Section 7 of Table 1 indicates four research programs which are continuing to advance the state-of-the-art for durability analysis and service life prediction. More detailed development of chemically based models for computer aided design and manufacture (CAD/CAM) of advanced composites is part of a continuing research program being conducted as an extension of this overview. In place of a redundant review of ASTM performance proof test methods the reader is referred to the detailed and continuously up-dated references on this important subject particularly developed for composite materials with commercial source and compiled test data.(1,2)

10.0 SUMMARY AND CONCLUSIONS

In lieu of a detailed summary and personal conclusion relative to this overview of characterization techniques this report furnishes in Appendix 1 the self explanatory results of an overview questionnaire on chemical characterization of composite reliability. It is evident from the questionnaire response that cure monitoring and management are of high importance to the investigators and that chemical characterization has already developed a more mature status. It is anticipated that these fields of investigation will be readily incorporated into a general life prediction program such as outlined by the flow chart of Fig. 9.

The descending flow chart of Fig. 9 is an outline of composite material interactions under UV radiation, hydrothermal cycling, and mechanical loading which leads to property changes, damage mechanisms, and results in diminished reliability and durability. The types of chemical, physical, and mechanical tests which accompany the several stages of degradation are listed on the right side of Fig. 9. While still in an early development stage a

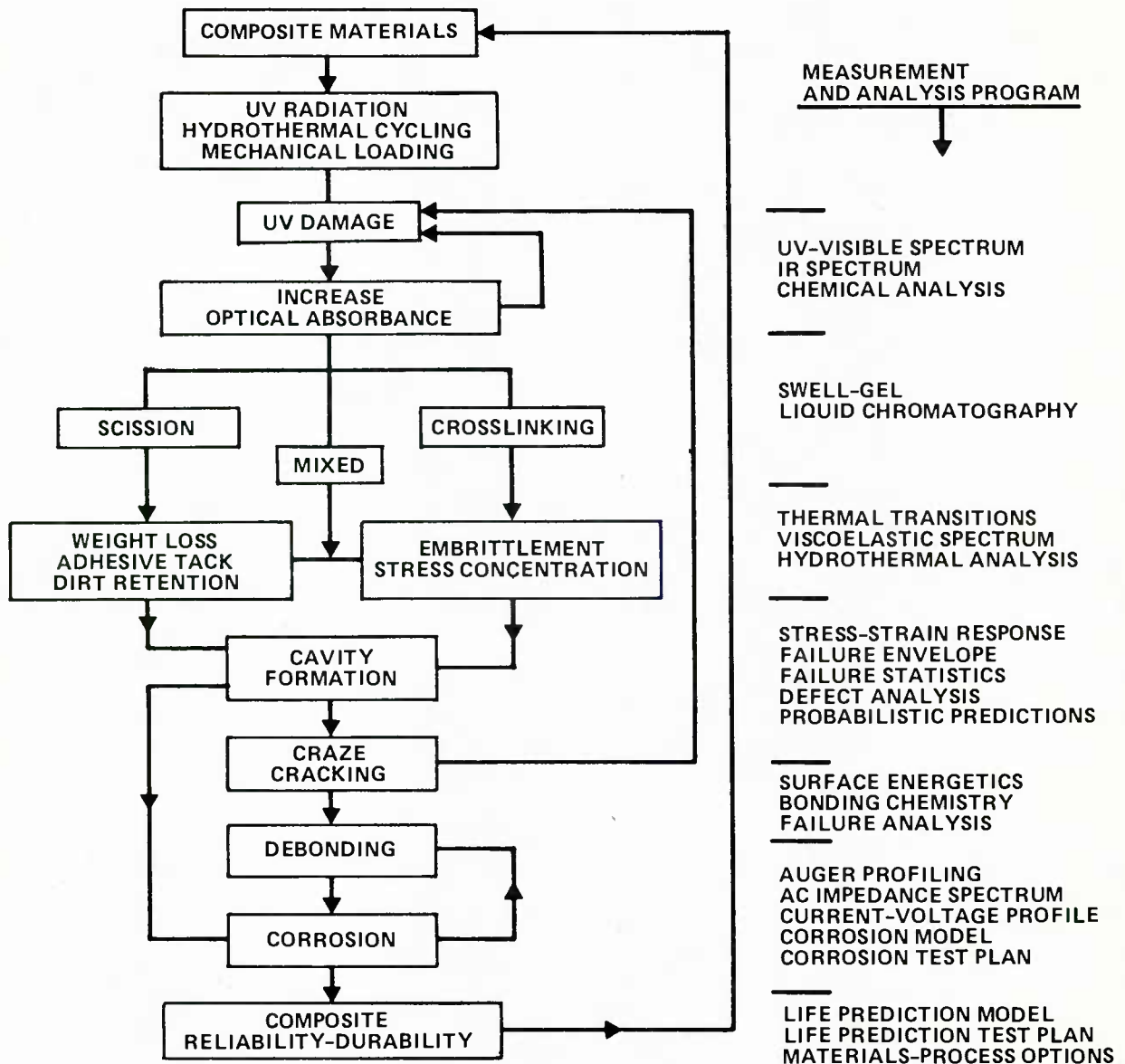


Fig. 9 General laminate life prediction program.

general laminate life prediction program which combines measurement and analysis appears to form an important avenue for future research. An important subject presented as a central issue in lower Fig. 9 is chemical corrosion degradation within the composite system. While this subject is only recently receiving detailed attention in composite life studies it appears to warrant increased attention in life prediction modelling.

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Report on Questionnaire for Chemical Characterization
of Composite Reliability

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On March 20, 1981 a questionnaire was sent to about 100 researchers active in the area of chemical characterization of polymer composites. The format of this questionnaire is shown in Table 1. The characterization methods covered by the questionnaire's field of interest were stated to include but not be restricted to:

1. elemental analysis
2. spectroscopy (IR, MS, NMR, atomic, all types)
3. chromatography (HPLC, GPC, GC, all types)
4. calorimetry
5. rheology (all types)
6. dielectrometry (all types)
7. relevant ASTM methods

The purpose of the survey is to present an overview of the subject: "Chemical Characterization of Composite Reliability" at:

1. The SAMPE National Symposium, Los Angeles, Calif., April 28, 1981.
2. The Critical Review: Techniques for Characterization of Composite Materials, Mass. Inst. of Technology, Cambridge, Mass., June 10, 1981.

On April 15, 1981 a compilation of 40 responses to the questionnaire was carried out and the results are summarized in Tables 2-6.

Before reviewing the survey results a note of explanation will clarify the meaning of the score system used to arrange the data in Tables 2-6. As noted in the questionnaire (Table 1) each question asks for a ranked list of five items in order of decreasing importance. For each question the following score rating was assigned:

1st choice score	= 5
2nd choice score	= 4
3rd choice score	= 3
4th choice score	= 2
5th choice score	= 1
higher choice score	= 0

These scores were summed over all questionnaires to produce the scores which appear in Tables 2-6. As an example, two first choices and a third choice from three questionnaires produce a summed score of 13.

As shown in Table 2 the survey shows a high score and current utilization of HPLC (high performance liquid chromatography) in chemical characterization of composites. Thermal analysis by calorimetry, gravimetric, and mechanical analysis is now closely complemented by rheological analysis of dynamic mechanical response. Infrared spectroscopy and other spectroscopic methods follow in importance as chemical characterization tools. Table 2 fairly clearly shows the present emphasis is on molecular separation and identification of polymeric constituents of composites followed closely by measurements relating to processability and process control.

The survey of presently most wanted chemical characterization methods shown in Table 3 shows the new emphasis on processability and process control. The high scores for rheological analysis reflects the importance of dynamic mechanical measurements in aiding process design. The second high score for dielectrometry evidently reflects the importance of this measurement as an in-process monitor of cure state. Interest in NMR (nuclear magnetic resonance)

which include C-13 and magic angle spin methods is indicated by a score comparable to thermal analysis and HPLC. The addition of mass spectroscopy analysis capability to both LC and GC follows and elemental analysis is evidently of increased interest in planned characterization. The relatively high scores given fracture mechanics and acoustic emission/ultrasonic methods shows the evident interest in connecting chemical characterization directly to mechanical reliability of composite response.

The survey of presently most used reference journals summarized in Table 4 shows that the more general publications of polymer engineering receive higher scores than the more specialized reference journals.

In contrast the survey of presently most used reference books shown in Table 5 shows that the more specialized textbooks appear to display greater usage and higher scores. The lists of Table 4 and Table 5 are quite informative and useful in providing a focus for general information availability on both chemical characterization and mechanical reliability of composites. These lists were developed from the first question of the questionnaire (Table 1).

The third category of response to the first question of the questionnaire provides the survey of presently most used specific reports and articles shown in Table 6. It is interesting to note the highest scores given personal communications and nonspecific contractor reports. This response, evidently indicates the importance of meetings, and current information exchange between research laboratories. Next in importance in specific research reports is a periodically revised and updated report edited by Lockheed Missiles & Space Co. Almost all the reports listed in Table 6 are less than five years old and this fact again reflects the evident importance of personal communication in keeping abreast of a rapidly expanding field of knowledge.

The results of this survey provide a sharply focussed overview of 40 expert opinions concerning the important field of chemical characterization of composite reliability. The survey summaries of Tables 2-6 represents the unedited compilation of the questionnaire responses.

Table 1: OVERVIEW QUESTIONNAIRE ON CHEMICAL CHARACTERIZATION
OF COMPOSITE RELIABILITY

- A. Please list five (or more) references (books, journals, specific reports, or articles) which you personally use in planning your characterization strategy (by all means reference your own research where applicable). List from 1 to 5 in order of decreasing importance.

- 1.
- 2.
- 3.
- 4.
- 5.

- B. Please list five instruments or characterization methods which you currently utilize and would want to retain over all others. List from 1 to 5 in order of decreasing importance.

- 1.
- 2.
- 3.
- 4.
- 5.

- C. Please list five instruments of characterization methods which you do not currently utilize and would want to obtain over all others. List from 1 to 5 in order of decreasing importance.

- 1.
- 2.
- 3.
- 4.
- 5.

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Rockwell International Science Center
1049 Camino Dos Rios
Thousand Oaks, CA 91360

Table 2: SURVEY OF PRESENTLY UTILIZED CHEMICAL
CHARACTERIZATION METHODS FOR 1981

<u>SCORE</u>	<u>Currently Utilized Methods</u>
142	HPLC (High Performance Liquid Chromatography)
87	Thermal Analysis
81	Rheological Analysis
55	Infrared Spectroscopy
42	Spectroscopy (General)
21	NMR (Nuclear Magnetic Resonance)
21	Mechanical Property
16	GC (Gas Chromatography)
13	Dielectrometry
11	TEM-SEM (Transmission-Scanning Electron Microscope)
10	ASTM Test
10	Mass Spectroscopy
9	Water Vapor Absorption
8	Elemental Analysis
7	Titration
4	Atomic Absorption
4	Specific Volume
3	Photoelasticity
2	Fracture Mechanics
1	X-ray Scattering

Table 3: SURVEY OF PRESENTLY MOST WANTED CHEMICAL
CHARACTERIZATION METHODS FOR 1981

<u>SCORE</u>	<u>CURRENTLY MOST WANTED METHODS</u>
105	Rheology Analysis
46	Dielectrometry
36	NMR (Nuclear Magnetic Resonance)
32	Thermal Analysis
28	HPLC (High Performance LC)
21	GC/MS (Gas Chromatography/Mass Spect.)
15	LC/MS (Liquid Chromatography/Mass Spect.)
13	Elemental Analysis
12	Fracture Mechanics
12	Acoustic Emission/Ultrasonics
12	TEM-SEM (Transmission-Scanning Electron Microscope)
9	Mechanical Testing
7	Computer Analysis
6	Raman Spectroscopy
5	Photoacoustic Spectroscopy
5	ESCA (Electron Spect. for Chemical Analysis)
5	TLC/FID (Thin Layer Chrom./Flame Ion Detection)
5	Surface Tension Analysis
5	X-ray Analysis
5	Spectroscopy (General)
5	ESR (Electron Spin Resonance Spect.)
5	Gas Chromatography
4	Titration
4	Polarized Fluorescence Spectroscopy
3	UV Spectroscopy
3	Atomic Absorption
2	Thin Layer Chromatography
1	Mass Spectroscopy
1	Chemiluminescence

Table 4: SURVEY OF PRESENTLY MOST USED REFERENCE JOURNALS FOR
COMPOSITE CHEMICAL CHARACTERIZATION FOR 1981

<u>SCORE</u>	<u>REFERENCE JOURNALS</u>
18	J. of Applied Polymer Science
10	Polymer Engineering and Science
10	SAMPE Proceedings
8	J. Polymer Science
7	Applied Spectroscopy
6	Analytical Chemistry
6	J. of Analytical Chemistry
4	J. of Chromatographic Science
4	Chemical Abstracts
4	Polymer Composites
4	J. of High Resolution Chromatography
3	J. of Liquid Chromatography
3	Thermal Analysis
2	J. of Polymer Technology
2	Plastics World
1	J. of Applied Polymer Technology
1	J. of Colloid and Interface Science
1	J. of Chromatography

Table 5: SURVEY OF PRESENTLY MOST USED REFERENCE BOOKS FOR COMPOSITE
CHEMICAL CHARACTERIZATION FOR 1981

<u>SCORE</u>	<u>REFERENCE BOOKS</u>
28	H. Lee and K. Neville, "Handbook of Epoxy Resins, McGraw-Hill, New York (1967)
22	ASTM Test Methods
10	P. Hedwig, "Dielectric Spectroscopy of Polymers," Halstead-Wiley, New York
10	D. H. Kaelble, Physical Chemistry of Adhesion, Wiley-Interscience, New York (1971)
6	L. J. Bellamy, "Infrared Spectra of Complex Molecules,"
6	C. A. May and T. Tanaka, "Epoxy Resins," Marcel Dekker, New York, (1973)
5	Enc. of Polymer Sci. & Tech.
5	Scott's Standard Methods of Chemical Analysis
5	Billmeyer, "Textbook of Polymer Science"
5	F. Wehrli and T. Wirthlin, "Interpretation of Carbon 13 NMR Spectra"
5	L. E. Nielsen, "Mechanical Properties of Polymers," Vol. 1, 2, Marcel Dekker, New York (1974)
4	MIL SPECS
4	Whorlow, "Rheological Techniques," John Wiley New York
4	L. R. Snyder and J. J. Kirkland, "Introduction to Modern Liquid Chromatography," Wiley, New York (1974)
4	McCrum, Read and Williams, "Anelastic and Dielectric Effects in Polymer Solids, Wiley, (1967)
4	C. A. May (Ed), "Resins for Aerospace," ACS Symposium Series 132 (1980)
4	Sadtler Spectral Catalogs

Table 5: (Continued)

<u>SCORE</u>	<u>REFERENCE BOOKS</u>
4	E. G. Brame, Jr., "Applications of Polymer Spectroscopy," (1978)
4	W. W. Yau, J. J. Kirkland, and D. D. Bly, "Modern Size Exclusion Liquid Chromatography, Wiley, New York (1979)
4	S. L. Rosen, Fundamental Principles of Polymeric Materials, Barnes and Nobel (1971)
3	NIOSH Manual of Analytical Methods
3	Test Manual-Institute of Interconnecting Packaging, Electronic Circuits
3	C. P. Smyth, "Dielectric Behavior of Structure," University Reprints
3	Polymer Handbook
3	SAE Specs.
3	I. M. Ward, "Mechanical Properties of Solid Polymers," Wiley-Interscience, New York (1971)
2	J. Urbanski, et al, "Handbook of Analysis of Synthetic Polymers and Plastics
2	Handbook of Fiberglass
2	G. P. Anderson, S. J. Bennett, and K. L. DeVries, "Analysis and Testing of Adhesive Bonds," Academic Press, New York (1977)
2	Van Krevelen, "Properties of Polymers"
1	J. V. Schmitz, et al (Eds.), "Testing of Polymers," Vol. 1-4, Wiley, New York
1	L. R. Snyder, "Principles of Adsorption Chromatography"
1	Deanin, "Polymer Structure Properties and Applications"

Table 6: SURVEY OF PRESENTLY MOST USED SPECIFIC REPORTS AND ARTICLES
FOR COMPOSITE CHEMICAL CHARACTERIZATION FOR 1981

<u>SCORE</u>	<u>SPECIFIC REPORTS AND ARTICLES</u>
20	Personal Communications
20	Contractor Reports, Nonspecific
16	D. K. Hadad (Ed.), "Chemical Quality Assurance Test Procedures for Advanced Composite Resin Matrices," Lockheed Missiles and Space Co., Inc., May 1980
15	AFML-TR-76-112
12	Instrument Manufacturer's Literature
8	J. F. Carpenter, "Quality Control of Structural Non-Metallics," U.S. Navy Contract No. N00019-76-C-0138, Final Report for Period Oct. 15, 1975 to Oct. 16, 1976
8	AFML-TR-77-217
5	J. F. Carpenter and T. T. Bartels, "Characterization and Control of Composite Prepregs and Adhesives," SAMPE Quarterly Jan. 1976
5	AFML-TR-79-4180
5	R. Hinrichs and J. M. Thuen, "Advanced Chemical Characterization Techniques Applied to Manufacturing Process Control." SAMPE Vol. 24, (May, 1979) p. 404
5	W. D. Bascom, J. L. Bitner, R. J. Moulton and A.R. Siebert, Composites, Jan. 1980, p. 9.
5	R. J. Morgan, Polym. Plastics Tech. and Eng., <u>10</u> , 49 (1978)
5	A. A. Wickham, D. D. Rice and R. J. DuBois, "Chemical Analysis of Composite Prepregs and Resins," 24th SAMPE Symposium (May 1979)
5	K. Kawata, S. Hashimoto, K. Kurokawa and N. Kanayama, "A New Testing Method for the Characterization of Materials in High Velocity Tension," in J. Harding Ed., Mechanical Properties at High Rates of Strain, Inst. of Physics, Bristol and London, 1979, p. 71-80
4	C. A. May, et al, SAMPE Symposium (1976), p. 274

Table 6 (continued)

<u>SCORE</u>	<u>SPECIFIC REPORTS AND ARTICLES</u>
4	K. Kawata, "Micromechanical Study of High Velocity Deformation of Solids," in 15th Int. Cong. of Theor. and Appl. Mech. (Editors: F.P.J. Rimrott and B. Tabarrock) North Holland Pub., (1980), p.307-317
4	Customer Specifications
4	H. Stenzenberg and M. Herzog, "Thermal Analytical Methods for Characterization of Resins, Pregregs and Composites, ESA Symp. on Spacecraft Materials (Oct. 1979).
4	Koutsky and Mijouie, Polymer, 20 (1979) p. 1095
4	G. L. Hagnauer, Waters Associates, Inc. Publ. J09/Oct. 1978
4	C. A. May, et al, SAMPE Symposium (1976) p. 274
4	R. Hinrichs, "Environmental Effects on the Control of Advanced Composites Material Processes," SAMPE Journal (Nov.-Dec. 1979), p. 12-20
4	A. G. Miller, P. E. Hertzberg and V. W. Rantala, "Toughness Testing of Composite Materials," SAMPE Preprints, <u>12</u> , 269 (1980)
4	AFML-TR-79-4166
3	E. L. McKague, J. Reynolds, and J. Halkias, "Swelling and Glass Transition of Epoxy Matrix Material in Humid Environments," J. App. Poly. Sci., <u>22</u> , (1978), p. 1643-1654
3	Progress Reports, Contract NASI-15371, Rockwell Int. Corp.
3	K. Kawata, A. Hondo, S. Hashimoto, N. Takeda, and H. L. Chung, "Dynamic Behavior Analysis of Composite Materials; Mechanics, Mechanical Properties and Fabrication, (Editors: K. Kawata and T. Akasaka), Japan Soc. of Composite Materials, Tokyo 1981 (in press)
3	J. S. Fritz, "Titration of Bases in Nonaqueous Solvents," Anal. Chem., <u>22</u> , 1028-1029 (1950)

Table 6 (continued)

<u>SCORE</u>	<u>SPECIFIC REPORTS AND ARTICLES</u>
3	D. H. Kaelble and P. J. Dynes, "Preventative Nondestructive Evaluation (PNDE) of Graphite Epoxy Composites," Ceramic Eng. and Sci. Proc., <u>1</u> , (1980), p. 458-472
3	"Thermal Analysis Review: Dynamic Mechanical Analysis (DuPont Instruments)
3	J. K. Gillham, "Formation and Properties of Network Polymeric Materials," Poly. Eng. and Sci., <u>19</u> (1979) p. 676
3	E. H. Andrews, "Developments in Polymer Fracture," Applied Science Publishers, London (1979)
3	C. A. May, T. D. Helminiak, and H. A. Newey, "Chemical Characterization Plan for Advanced Composite Prepregs," 8th Nat. SAMPE Tech. Conf. (Oct. 1976)
3	R. E. Trujillo and B. P. Engler, Sandia Nat'l. Lab Report No. SAND78-1504
2	J. F. Carpenter, "Test Program Evaluation of 3501-6 Resin," Naval Air Systems Command Contract # N0019-77-C0155, Final Report, May 1978
2	E. L. McKagaue, J. Reynolds, and J. Halkias, "Moisture Diffusion in Fiber Reinforced Plastics," ASME J. of Eng. Material and Tech., <u>98</u> H <u>1</u> , (Jan. 1976) p. 92
2	W. Wendlandt, "Thermal Methods of Analysis," in Chemical Analysis, Vol. 19, Wiley, New York, 1974
2	12th National SAMPE Tech. Conf. Vol. 12 (1980)
1	Manson, Sperling, and Kim, AFML-TR-77-124
1	"Chemical Fingerprinting of Composite Materials," SME Tech. Paper EM-78-403
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This overview of characterization techniques for composite reliability describes the recent highly organized advancement in the methods and management of characterization methodologies. These characterization methodologies can be listed in the order of their implementation as follows: 1) chemical quality assurance testing, 2) processibility testing, 3) cure monitoring and management, 4) non-destructive evaluation, 5) performance and proof testing, and 6) durability analysis and service life testing. This overview discusses the detailed methods in the context of the management concept for implementing the specific tests. This report presents the results of an overview survey concerning "Chemical Characterization for Composite Reliability."

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